

Title	TRACE ELEMENTS IN TREE STEMS(Dissertation_全文)
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Citation	Kyoto University (京都大学)
Issue Date	1990-03-23
URL	http://dx.doi.org/10.14989/doctor.k4571
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Type	Thesis or Dissertation
Textversion	author

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TRACE ELEMENTS IN TREE STEMS

1990

NAOKI OKADA

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Introduction

Plant body contains of many kind of elements which were absorbed during the growth. Such elements comprises both essential and nonessential ones, and their kind and amount show wide variety according to the species and the growing condition (Bowen 1979a). Carbon, hydrogen and oxygen are the major elements of the elementary constituents of cell. Nitrogen, phosphor, potassium and calcium, which are present in a relatively large quantity in most organisms, have been studied rather well. However, function and significance of other trace elements, some of which are indispensable elements of enzyme or other organic substances (Hewitt and Smith 1975), have not been extensively studied.

The role of trace elements on plant body has been studied in the field of plant nutrition, mainly on herbaceous plants. The herbaceous plants are generally small in size, and their life cycle is short, and therefore are easier to study than trees themselves. These are the reasons why herbaceous plants have been exclusively studied. This, consequently, has hampered the study on trace elements in trees.

However, there is a limitation in the methodology which was applied the result obtained from herbaceous plants to trees. Because trees have acquired their particular life type through the evolution, their physiological nature would be different from that of herbaceous plants accordingly. This problem will be resolved only by using trees.

In addition, the metabolism of trace elements in

plants show wide variety. In general, 16 elements are confirmed to be essential to the higher plants (Kumazawa 1981), but other elements are also beneficial and substitutable. Some plants accumulate a certain element in extraordinarily high concentration under the ordinary condition, whereas others adapt themselves under high concentration of salts. The former is called the accumulator plants (Nishimura 1989), and the latter the halophytes (Bowen 1979b). Both provides an important view on the function of elements and the inherent nature of metabolism in plants.

On the other hand, there is another approach from environmental science. Trees grow for a long period, and time at which the xylem was formed can be identified by annual ring. These are preferable properties for study of the chronological change in the environment. Dendrochronology has enlarged the applicable field, not only archaeological and meteorological point of view, but also the estimating of human impact and other earth and environmental science (Noda 1988, 1989).

In these aspects, the method which surveys the element concentration in annual rings to examine the chemical history of the environment has been attempted with development of analytical method. However, fundamental data is still insufficient owing to lack of the information of natural background of pollutants, route of uptake and translocation in plants, metabolic property of each species, and so on.

In the present study, the radial distributions of trace elements in stem of many trees was measured by means of instrumental neutron activation analysis

(INAA). One of the purposes in the present study is to investigate behavior of elements in stem, such as translocation and accumulation, relation between elements and heartwood formation, and metabolic property of each species. Another purpose is to examine potential in using trees as an indicator of environmental pollution. The term "trace elements" usually has two meanings, one is the minor nutrient elements in the field of plant nutrition, and the other is a trace quantity of elements in analytical chemistry. In the present study, it is used as the latter meaning.

In chapter 1 the author surveys the distribution of trace elements in stem of sugi (Cryptomeria japonica D. Don) and discuss the factors affecting their distribution, such as position in the stem, tree age, growing condition, etc. In chapters 2 and 3, radial distributions of trace elements in stems of representative soft- and hardwood species grown in Japan are described.

Chapter 1 Distribution of trace elements in stem of sugi (Cryptomeria japonica D. Don)

1.1 Introduction

The elements in the stems of trees have been studied generally in two aspects as mentioned in the general introduction, i.e. plant physiology/nutrition and environmental study.

In the first aspect, content of the nutrient elements, such as N, P, K, Ca and Mg, in the stems of many trees have been reported (Furukawa 1961, 1963, 1964; Tsutsumi 1965; Harada and Sato 1966). Most of these studies have been mainly focused on estimations of amount of major nutrient elements in stems and the circulation of these elements in forests. Other trace elements in stems of trees have attracted little attention, though some of them are physiologically important.

In the second aspect, the distributions of heavy metals (Szopa et al. 1973; Suzuki 1975, 1981; Kardell and Larsson 1978) and other pollutants (Ogihara and Katsuno 1984; Katayama et al. 1986b; Kohno et al. 1988; Chigira et al. 1988) in the annual rings have been measured to detect chronological changes in environmental pollution. However, the utility of the tree-ring method is not fully agreed (Rolf 1974). Lepp (1975) pointed out that the following knowledge required to apply this method to heavy metal pollution: the transport form of metals and other organic ligands, the mobility of metals and lateral redistribution of metals via xylem rays.

At the present stage of trace elements study in

trees, little is known about the content in stem of each species and affecting factor on their uptake. However, considering the largest contribution of trees to the total biomass of plants and their potential in environmental science, the accumulation of fundamental data on trace elements has become increasingly important. This chapter describes the distributions of trace elements in stem of sugi (Cryptomeria japonica D. Don) and discusses what factors affect their uptake and translocation.

1.2 Experimental

1.2.1 Materials

Three different sampling methods were taken to compare growing condition, tree age and partition of elements between sap and wood substance.

(a) Comparison of growing condition

Sample sugi trees were collected in two areas (Table 1.1): the Ashu Experimental Forest, Kyoto

Table 1.1 Description of sample trees growing under different conditions.

Sample tree	Site	D.B.H. ^{a)} (cm)	Tree age	No. of sapwood rings
Ashu	Ashu Exp. Forest (Kyoto Pref.)	65	115	15
Tokuyama	Tokuyama Exp. Forest (Yamaguchi Pref.)	32	63	18

a) Diameter at breast height.

University (Kyoto Prefecture), and the Tokuyama Experimental Forest, Kyoto University (Yamaguchi Prefecture). The Ashu sugi was almost free from influence of human activities, whereas the Tokuyama sugi was growing close to an industrial area.

Sample disks (20 cm thick) were cut at the breast height, from which sample blocks from the pith to the cambium were taken. After oven-drying under a mild condition (40-60 °C , 1 week), each block was cut into single or multi-year sections in portions of narrow ring width. Each section (about 300 mg) was then oven-dried at 105 °C for 24 hours and weighed. Thirteen sections from the Ashu sugi and 14 from the Tokuyama sugi were analyzed.

The bark of the two sample trees was also analyzed. After removing the outer surface to avoid contamination, each bark sample was cut into 4- or 5-year sections. The dating of the bark was done according to the number of bast fibers (Miyagawa et al. 1973). Five sections were cut from the Ashu tree and 4 sections from the Tokuyama tree; 2 sections of each tree were inner bark.

To estimate availability of elements, surface soil (A layer) at each sampling site was also collected. Soil samples were oven-dried at 105 °C for 48 hours, and the fractions passing through a 2 mm sieve were used. A part of each soil was ground with an agate mortar, and 15 mg of each was analyzed. In addition, 5 g of each soil was extracted with 100 ml of 1 N ammonium acetate solution for 2 hours. Then, 50 ml of each filtrate was evaporated, and the residue was analyzed.

(b) Comparison of tree age

Six sugi trees (A-F) were sampled in the Ashu Experimental Forest of Kyoto University, Kyoto Prefecture, of which Tree D was cut down in July and others in June, 1980 (Ashu-sugi; Table 1.2). Their ages ranged from 2 to 60 years, and the disks of Trees A, B and C contained no heartwood. The sample disks of Trees D, E and F were cut at breast height, and those of Trees A, B and C were taken just below the crowns because of their shorter height.

The sample preparation for elemental analysis was the same as the previous section.

Table 1.2 Description of sample trees of different ages (ashu sugi).

Sample tree	Height (m)	Diameter (cm)	Sapwood width (cm)	Number of annual rings	
				Total	Heartwood
A	0.8	1.4	0.7	2	- a)
B	1.0	2.3	1.2	4	- a)
C	2.2	4.1	2.1	13	- a)
D	- b)	7.8	3.6	23	4
E	4.0	8.5	3.4	34	11
F	5.0	10.0	1.6	60	17

a) Including no heartwood.

b) Uncertain.

Table 1.3 Sample trees extracted sap (Ashu sugi).

Sample	Height (m)	D.B.H. (cm)	Tree age
Tree G	12	25	90
Tree R	17	27	149

(c) Comparison of partition of elements between sap and wood substance

Two sample sugi trees were obtained in the growing season (20 May 1982) and another in the resting season (19 November 1981), respectively, from the Ashu Experimental Forest, Kyoto University (Table 1.3). They are abbreviated "Tree G" and "Tree R", respectively. Sample disks (30 cm thick) were cut every 3 m from the breast height upward. The disks were wrapped with polyethylene film to prevent from evaporation and immediately were brought to the laboratory for further preparation.

A block, 3 cm (T) \times 4.5 cm (L) was cut from each sample disk, and sections of 1 cm thick in the radial direction were cut from each block from the cambium to the pith. The saw-cut surfaces of each section were flaked with a knife to avoid contamination.

The xylem sap was squeezed mechanically from each section with a vise and collected in a polyethylene tube. The amount of sap obtained from one section was 1 - 5 g. After squeezing, each section was weighed, oven-dried at 105 °C for 48 hours, and weighed again to estimate the moisture content.

The sap samples were placed in limited amounts on sheets of filter paper (Toyo, No. 5B) and evaporated with an infrared lamp (250 W). The wood samples (300 - 400 mg) were taken from the wood sections from which the sap had been extracted. The sample preparation for elemental analysis was described in the previous section.

In the present study, the tissue free from the sap was called "wood substance". The concentration of an

element in wood substance (C_{sub}) was calculated from the total content of the element in the tissue (C_{tot}), the element content in the xylem sap (C_{sap}), and the moisture content of the tissue (u) as follows:

$$C_{sub} = C_{tot} - C_{sap} \times \frac{(u - 28)}{100}.$$

In this calculation, the water corresponding to that up to the fiber saturation point (28%) was excluded from the xylem sap, because it was not free water.

1.2.2 Determination of elements

Instrumental neutron activation analysis (INAA) was applied to determination of trace elements. Kyoto University Reactor (KUR, thermal neutron flux: $2.2 \times 10^{13} \text{ n/cm}^2/\text{s}$) in the Research Reactor Institute, Kyoto University and TRIGA Mark II type reactor (thermal neutron flux: $4 \times 10^{12} \text{ n/cm}^2/\text{s}$) in the Institute of Atomic Energy, Rikkyo University were used for the neutron irradiation.

For the analysis of short-lived nuclides (Al, V, Ca, Mg, Mn, Cl, Na and K) samples were irradiated by thermal neutron flux for 2 - 5 min, and then the induced γ ray was measured for 200 - 300 sec with an intrinsic Ge(Li) detector coupled with 4K channel MCA (CANBERRA) after 2 - 5 min cooling. Middle- and long-lived nuclides (Br, La, Sm, Rb, Cs, Ba, Co, Zn, Ce and Sb) were determined by irradiating samples for 1 hour by thermal neutron flux, and then the induced γ ray was measured twice for 3000 - 10000 sec after cooling samples for 1 week and 3 weeks. Gamma ray spectrometry of middle- and long-lived nuclides was done with a

Ge(Li) detector (HORIBA) with 2K channel MCA (NORTHERN) at the Radioisotope Research Center, Kyoto University.

The further details of procedure were described in elsewhere (Katayama et al. 1986a).

1.3 Results and discussion

1.3.1 Radial distribution of trace elements in stem

(a) Radial distribution in xylem

Although absolute amount of each element was found to be different between Ashu sugi and Tokuyama sugi, the distribution patterns for a single element were similar in both trees. The same trend was also reported (Katayama 1986a).

Alkali metals

The concentrations of Na, K and Rb were virtually constant across the heartwood region. However, at the boundary between the heartwood and sapwood, abrupt concentration decrease was noticed and again the concentration increased close to the cambium (Fig. 1.1). Among these elements, K and Rb gave a good correlations for logarithms of their concentrations (Ashu sugi: $r = 0.972$, Tokuyama sugi: $r = 0.910$; significant at the 99.9% confidence level) compared with other elements studied. Cesium, although omitted from Fig. 1.1, had a pattern similar to those of the other alkali metals, reported in previous papers (Katayama et al. 1986a, 1986b). Furthermore, this pattern of alkali metals in sugi was also observed by Furukawa (1964) for K and by Taneda et al. (1986) for Na and K. Therefore, this must be a common distribution pattern of of alkali metals in mature sugi.

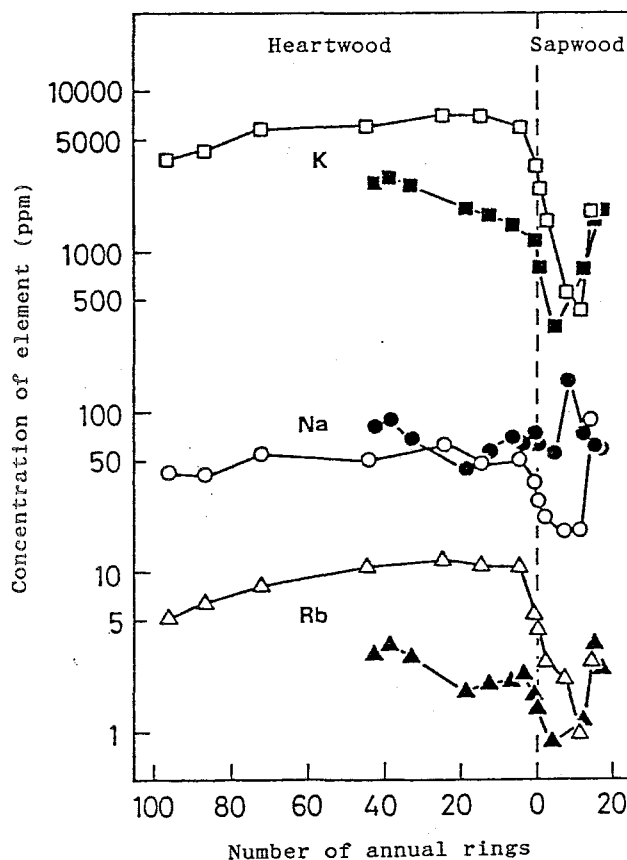


Fig. 1.1 Radial distributions of K, Na and Rb in stem of sugi.

Note: White and black symbols represent Ashu and Tokuyama, respectively.

Although K and Rb in the heartwood and inner sapwood had large difference in their concentrations between the two sample trees, there was little difference near the cambium. The outermost part of the xylem, where the tissue is alive, appears to be under homeostatic regulation.

Alkaline earth metals

The radial distribution pattern of Mg was similar

to that of alkali metals, whereas that of Ca did not have the abrupt change in its concentration across the boundary between the heartwood and sapwood portions (Fig. 1.2).

Magnesium was found to have a much greater correlation with K and Rb than with Ca in this and a previous study (Katayama *et al.* 1986a). When the data collected by Taneda *et al.* (1986) was reexamined, a good correlation between Mg and K was observed. The chemical properties of Mg are more similar to those of the alkali metals than to those of Ca, although it belongs to the II a group in the periodic table. Indeed, the behavior of Mg in plants is quite different from that of Ca. While Mg is easily translocated and functions as the activator of many enzymes, Ca is very immobile and has a structural function in the cell (Kawasaski 1981, Epstein 1972b).

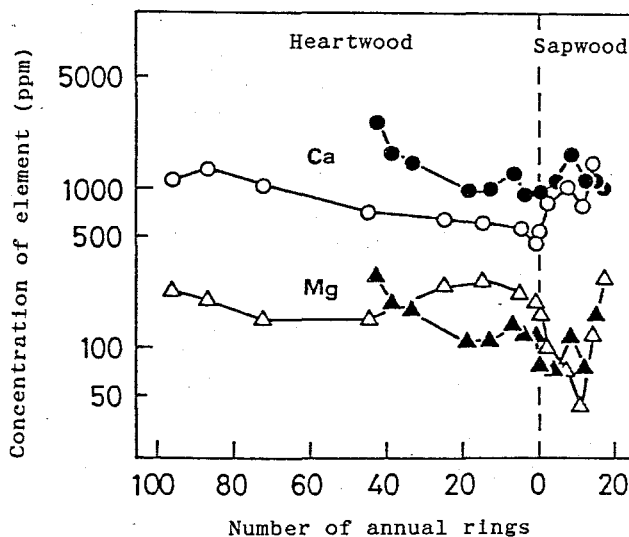


Fig. 1.2 Radial distributions of Mg and Ca in stem of sugi.

Note: Note is same as in Fig. 1.1.

Other metals

The concentration of Mn was found to remain unchanged across the heartwood but increased near the cambium (Fig. 1.3). This finding of the concentration increase toward the the cambium in the sapwood is consistent with that in a previous report (Katayama et al. 1986a). As also observed by Taneda et al. (1986), the Mn concentration in the xylem of sugi is generally increased in the sapwood region toward the cambium.

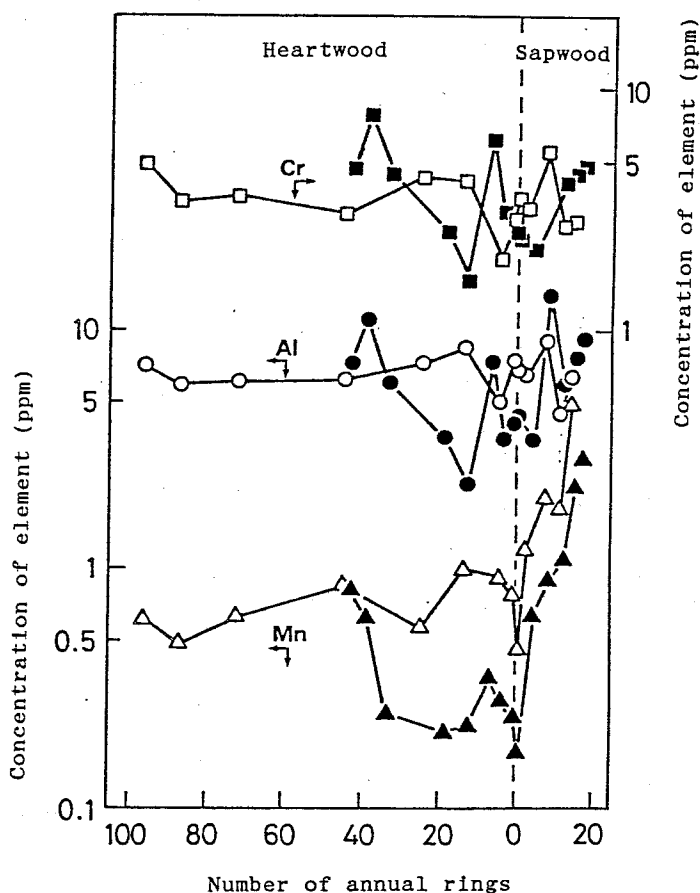


Fig. 1.3 Radial distributions of Cr, Al and Mn in stem of sugi.

Note: Note is same as in Fig. 1.1.

Neither of Al and chromium neither showed any similarity in distribution between the two sample trees nor any particular tendency in each sample tree (Fig. 1.3).

Other metals were below the detection limit in several samples. Their radial distribution patterns did not indicate any significant trends: these metals varied almost at random within limited range. Antimony was not detected in most of the samples.

Halogens

It was found that Cl and Br were basically the same in their concentrations across the heartwood. However, they increased their concentrations toward the cambium in the sapwood (Fig. 1.4). They gave a good

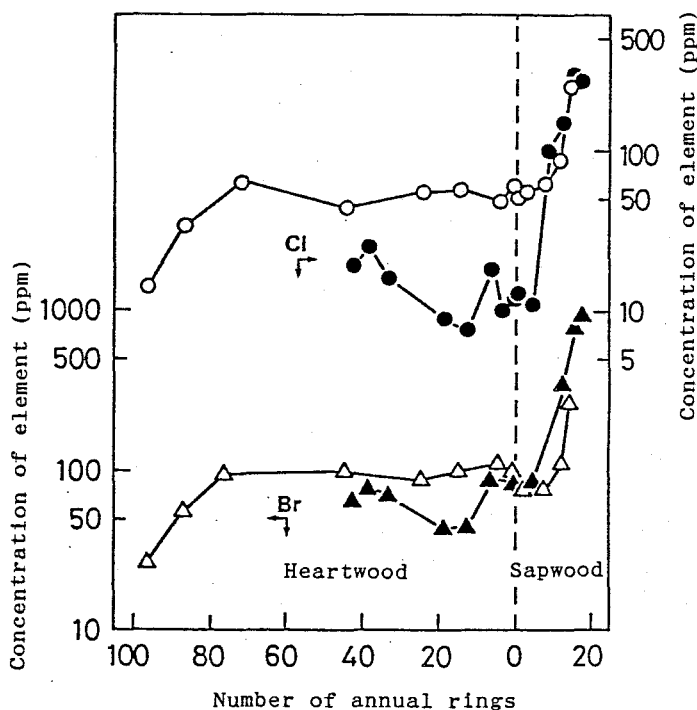


Fig. 1.4 Radial distributions of Cl and Br in stem of sugi.

Note: Note is same as in Fig. 1.1.

correlation for logarithms of their concentrations (Ashu sugi: $r = 0.944$, Tokuyama sugi: $r = 0.974$; both are significant at the 99.9% confidence level).

The concentration changes near the pith typically seen for halogens, a decline in Ashu sugi and an increase in Tokuyama sugi, were also observed for other elements in Tokuyama sugi. A similar trend near the pith was found in many tree species investigated by Furukawa (1961, 1963). Galligan *et al.* (1965) pointed out that a similar change of Mn concentration in Douglas fir (Pseudotsuga menziesii (Mirb.) Franco) appeared to correspond to change from juvenility to maturity.

The concentration levels of these two elements varied over a wide range of at least 10 times or more in each sample tree. This variation is probably due to their chemical forms. Chlorine usually exists as an ion and is very mobile in plants (Kouchi 1981). The same arguments probably are valid for bromine also.

(b) Radial distribution in bark

The features of the element distributions in bark were quite different from those in xylem: the elements of the same group did not necessarily have similar distribution patterns (for example, Na and K; Cl and Br) and most of the elements were more abundant in bark than in xylem (Figs. 1.5 to 1.8).

Three types of distribution patterns from the innerbark to the outerbark were found; i.e., Type 1: concentrations increased toward the outside (Na, V, Al and Br), Type 2: concentration decreased toward the outside (K), and Type 3: concentration first decreased and

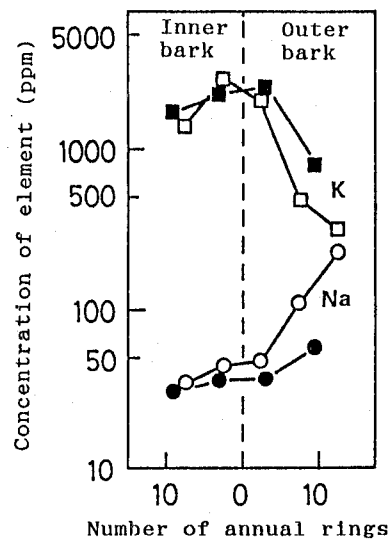


Fig. 1.5 Radial distributions of K and Na in bark of sugi.

Note: Note is same as in Fig. 1.1.

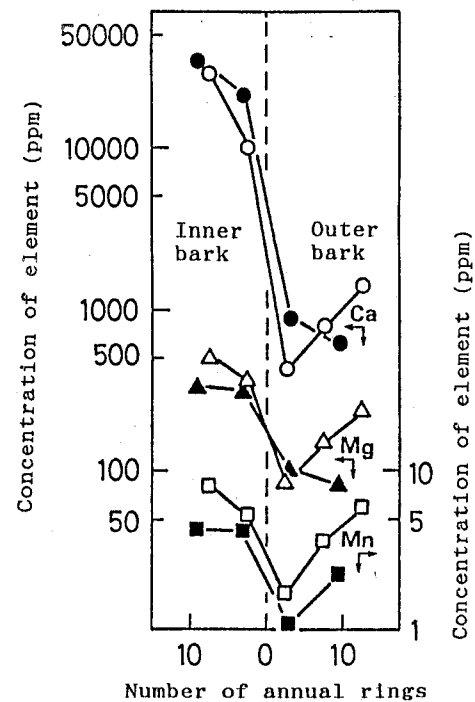


Fig. 1.6 Radial distributions of Mg, Ca and Mn in bark of sugi.

Note: Note is same as in Fig. 1.1

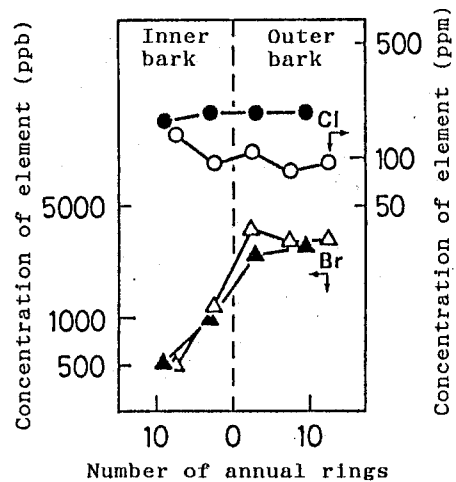


Fig. 1.7 Radial distributions of V and Al in bark of sugi.

Note: Note is same as in Fig. 1.1.

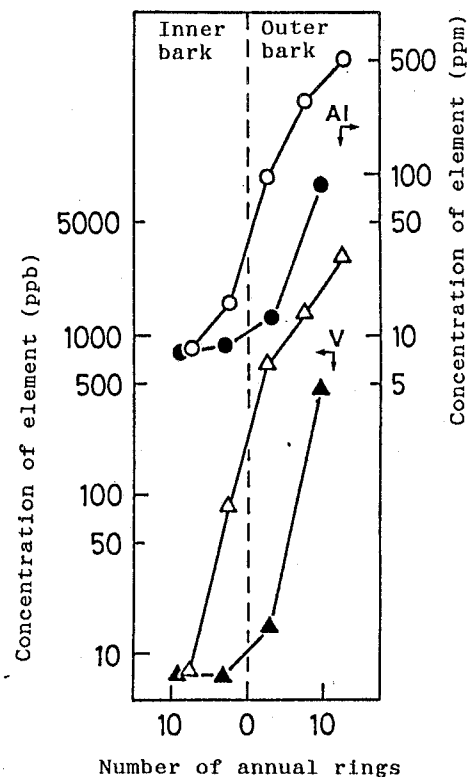


Fig. 1.8 Radial distributions of Cl and Br in bark of sugi.

Note: Note is same as in Fig. 1.1.

then increased (Mg, Ca and Mn). In addition, the following elements, which are not shown in the figures, were found to belong to these three types: Type 1: Sc, Ti, La, Sm and Fe; Type 2: Rb; and Type 3: Co. Only the concentration of chlorine, differing from other elements investigated, stayed almost constant.

Most of the nutrient elements analyzed belong to Types 2 or 3, whereas elements in Type 1 are not confirmed to be essential for plants, except Fe. Bark tissue may thus tend to retain beneficial elements and to discharge.

The elements of Type 1 rarely occur in plants, but soil is relatively rich in them. Therefore, the larger concentrations of such elements in the outermost bark are probably caused in part by the adhesion of aerosols originated from the soil.

(c) Factors influencing distribution of trace elements
Physiological processes

Many elements that were investigated have common features in their radial distribution patterns, i.e., almost constant in the heartwood, the increase/decrease at the sapwood-heartwood boundary, and then the increase toward the cambium.

Since there is no living tissue in the heartwood, physiological reactions are considered not to occur there. This seems to be the reason why concentrations of many elements are almost constant in the heartwood.

The changes in the concentrations of elements around the sapwood-heartwood boundary, for example, the decrease of alkali metals and Mg across the boundary toward the outer part and the increase of Mn and Cl

from the boundary to the cambium, are likely to be brought about during the heartwood formation process. These changes are probably caused simply by changes in the physicochemical state of the tissue, such as the production of heartwood substances and the increase/decrease of pH value. This hypothesis is supported by the fact that the above changes are not specific for a particular element but are common to those elements with similar chemical properties, such as the alkali metals or the halogens. This, however, does not necessarily mean that no elements play a particular role during heartwood formation.

The concentration levels of K, Rb, Mn and Cl in the heartwood differed greatly between two sample trees. Nevertheless, the values near the cambium were close regardless of age and growing site. This suggests that there is a regulating mechanism in living tissue, although a wide range of elemental concentrations appears in heartwood where there is no living tissue.

The greater concentration values of alkali metals and Mg in the heartwood than in the sapwood is probably related to their electrochemical role. The pH of sugi is lower in the sapwood than in the heartwood (Goto and Ohnishi 1967). This seems contradictory to the production of polyphenols (which are weak acids) in the heartwood. As Furukawa (1961) also stated, the above elements are likely to act on the regulation of pH as counter ions for organic acids. Indeed, the radial distribution patterns of several heartwood phenols reported by Nobuchi et al. (1985) are similar to those of alkali metals.

Environment

The uptake of elements into plants occurs mainly through the roots and partly through the surface of the above-ground parts. In the former case, the soil is the source of the elements; in the latter, rain and aerosols supply the elements.

Table 1.4 shows the elemental compositions of surface soils at the sampling sites and the amounts of 1N $\text{CH}_3\text{COONH}_4$ aqueous extractives. Although the sampling sites were selected considering the influence of human activities, the difference in the elemental compositions for the soils at these two sites was not as great as expected. Consequently, soil composition did not appear to make much difference between Ashu sugi and Tokuyama sugi. Under ordinary soil conditions, the uptake of elements via roots is regulated strictly.

Since bark is exposed to the atmosphere, it was expected that it would be more sensitive to changes than xylem in the environment. However, the analytical results do not provide clear evidence of the influence of human activities. On the contrary, the level of vanadium, which is released by the combustion of petroleum, was greater in the bark of Ashu sugi than in that of Tokuyama sugi which had grown near an industrial area. The xylem of sugi probably is not so sensitive to changes in environment, unless the change is drastic.

One of the concerns in this study was whether or not trees can be used as indicators of environmental pollution. To use trees for monitoring chronological changes of pollution, it is necessary that they accumulate the pollutants only in the annual ring formed in that season. To examine this, analytical results of

Table 1.4 Elemental composition of soils and 1 N ammonium acetate extractives at sampling sites.

Sample	Site	Elemental concentration (ppm)											
		Na	K	Mg	Ca	Ti	V	Mn	La	Sm	Al	Cl	Br
Soil	A	2300	19000	27000	3000	16000	120	890	38	4.6	89000	250	33
	T	7700	18000	27000	12000	9300	120	1500	23	3.7	73000	110	Tr.
Extractives ^{a)}	A	18	130	61	350	15	0.023	89	0.023	0.015	23	11	1.7
	T	24	Tr.	67	1300	1.8	0.017	32	0.069	0.015	4.9	3.6	0.40

A: Ashu, T: Tokuyama, Tr.: trace.

a) Microgram extracted per gram of soil.

Table 1.5 Element content in xylem of different sides of Ashu sugi.

Sample	Year formed	Element (ppm)							
		Na	K	Rb	Mg	Ca	Mn	Cl	Br
A1	(1966)	28	1300	2.2	92	530	0.85	22	84
A2	(1966)	46	4100	5.5	140	540	1.2	57	120
A3	(1963)	37	3500	5.5	190	440	0.79	59	99

Notes: A1 and A3 are in the same direction (south east), and A2 is opposite to them (north west). A2 and A3 are from heartwood, and A1 is from sapwood.

samples from the opposite sides, in a single annual ring, of Ashu sugi were compared (Table 1.5). Samples A1 and A3 are sapwood and heartwood, respectively, from the same side (South east) of the tree. Sample A2, on the opposite side (North west) from A1, came from the same annual ring as A1 but already had become heartwood.

As seen in the table, A2 is different from A1 and is similar to A3 in elemental concentrations. This indicates the following: 1) elements absorbed are not distributed homogeneously in a single annual ring and 2) the concentration values of some elements change during heartwood formation. The second point is also supported by the distributions of radionuclides, ^{137}Cs and ^{40}K , reported by Brownridge (1984) and by Katayama et al. (1986b). Consequently, in addition to what Lepp (1975) has pointed out, further studies on the behavior of each element during the formation of heartwood are required to establish the tree ring method.

1.3.2 Influence of tree age on the distribution of trace elements

(a) Radial distributions of trace elements in trees of various ages

The radial distributions of the trace elements in a series of tree ages of Ashu sugi (Trees D, E, and F; Figs. 1.9 and 1.10) showed a similarity to those in mature Ashu sugi described in the previous section: i.e., 1) K and Mg decreased from the outer heartwood to the adjacent sapwood and then increased when close to the cambium, 2) Mn and Cl increased toward the cambium in the sapwood region, and 3) Ca, not shown in the

Figures, did not abruptly increase/decrease even near the sapwood-heartwood boundary and was almost constant.

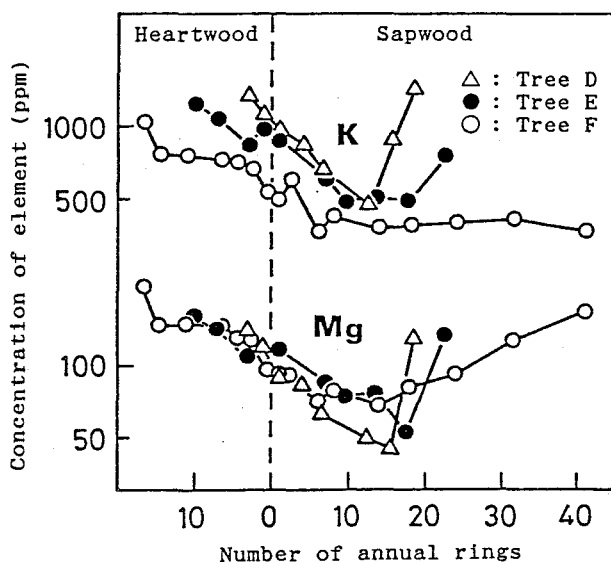


Fig. 1.9 Radial distributions of K and Mg in stem of Ashu sugi.

Another feature described in section 1.3.1 was that the most elements were distributed evenly in the heartwood. This did not appear conspicuously in this experiment. This is attributable to few heartwood rings in the samples. Figure 1.9 shows that the distributions of K and Mg in the heartwood became flat in the order of Trees D, E, and F, in accordance with increasing tree age.

Tree F included more than 40 rings in the sapwood which is considerably more than in normal sugi. As also seen from the narrow sapwood width, Tree F was suppressed, and this seemed to influence the distribution of the elements. For example, the concentrations of Mg, Mn, and Cl in the outermost sapwood in Tree F

did not increase as rapidly as those in Trees D and E. In addition, that of K was flat in the same region.

Many elements, other than those described above, scarcely were detected. Poor growth, as represented by Tree F, seemed to be correlated to small amounts of trace elements. Furukawa (1961) referred to the small content of nutrient elements in the stems of sugi when it grows poorly. Because of limited analytical precision, the radial distributions of low-level elements

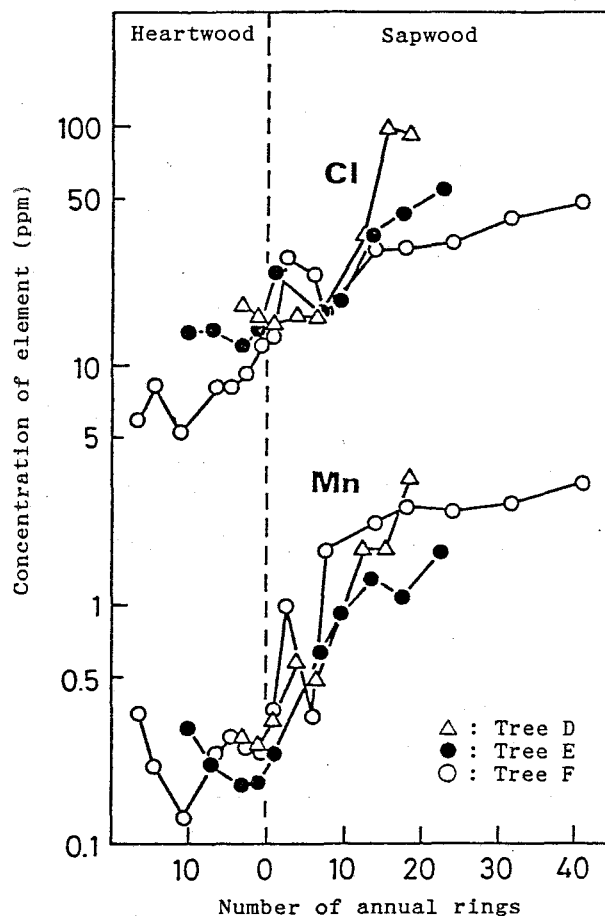


Fig. 1.10 Radial distributions of Mn and Cl in stem of Ashu sugi.

had no clear patterns. The smaller correlations, between Na and K and between Br and Cl in three trees, than those in section 1.3.1 probably can be attributed to the same reason.

(b) Growth of trees and the distributions of trace elements in the stems

From the findings discussed above, the elements in a stem probably vary their amounts during physiological changes such as aging and heartwood formation. Because it was difficult to survey such changes in a single tree, several trees were compared each other in the present study.

The radial distribution of K, Mn and Cl in Tokuyama sugi are shown as a plot of content of same elements in the piths of six Ashu sugi (A-F) against their ages (Fig. 1.11). Note that the sampling site was different in Tokuyama sugi and Trees A-F, and that the sampling position was different in Trees A-C (just below the crown) and E-F (at breast height). In spite of these differences, the amounts of these three elements in six Ashu sugi at different growing stages paralleled those in Tokuyama sugi. This also supports the previous hypothesis that physiological changes are reflected in the element amounts in a tree.

1.3.3 Element content in xylem sap and wood substance

(a) Element content in xylem sap

The following elements were determined with sufficient accuracy in xylem sap: alkali metals (Na, K, Rb and Cs), alkaline earth metals (Mg and Ca), Mn, and Cl. Copper and Br were sometimes detected. Each element

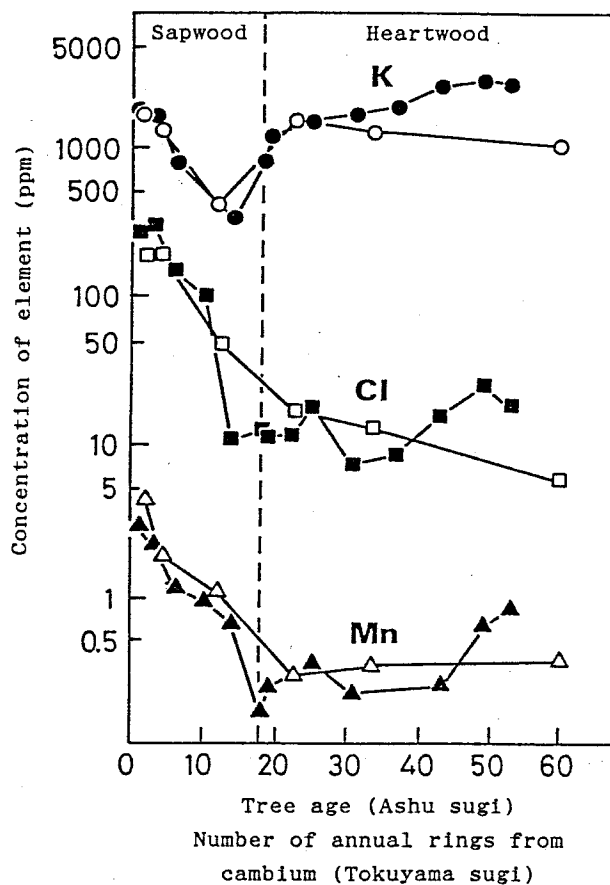


Fig. 1.11 Concentrations of K, Mn, and Cl in piths of six Ashu sugi and at breast height of Tokuyama sugi.

Notes: White and black symbols represent Ashu sugi and Tokuyama sugi, respectively. Dashed line indicates the sapwood-heartwood boundary of Tokuyama sugi.

distributed similarly in the radial direction at any stem height, and hence the feature at breast height mainly is described here.

Alkali metals (Na, K and Rb) were distributed evenly in the heartwood and abruptly decreased across the sapwood-heartwood boundary (Fig. 1.12). They reached a minimum at the center of the sapwood in Tree G and in the outermost sapwood in Tree R. The radial pattern of Cs was almost similar to those of the other alkali metals described above.

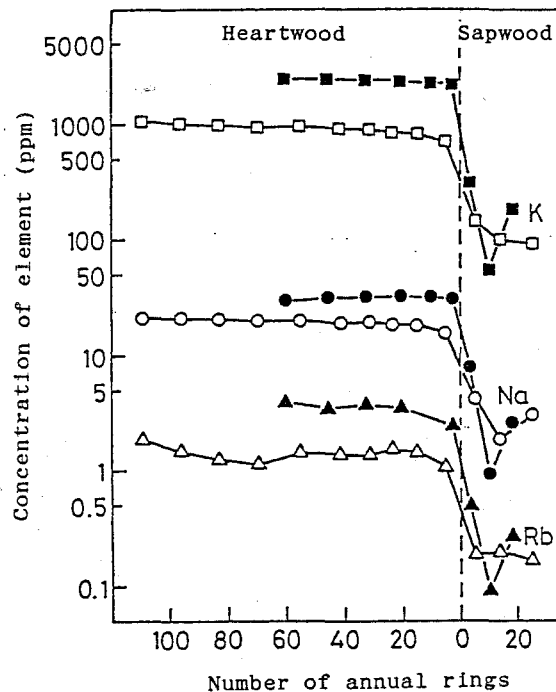


Fig. 1.12 Radial distributions of Na, K and Rb in xylem sap at breast height of sugi.
Note: Black and white symbols represent Tree G and Tree R, respectively.

Of alkaline earth metals, Mg was distributed similarly to alkali metals (Fig. 1.13). While concentration of Ca in Tree G decreased outwards across the sapwood-heartwood boundary as did those of alkali metals and Mg, it gradually increased outwards in Tree R. The variance of the Ca concentration was much smaller than that of the other elements detected.

The concentrations of Mn and Cl were greater in the sapwood than in the heartwood (Fig. 1.14). As seen also from Fig. 1.15, there was a peak of Cl concentration in the white zone. It decreased once and rose again towards the cambium. This trend was observed at other stem heights and was more conspicuous in Tree G than in Tree R.

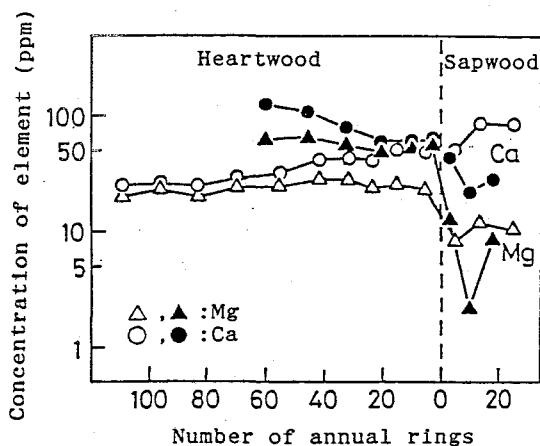


Fig. 1.13 Radial distributions of Mg and Ca in xylem sap at breast height of sugi.

Note: Note is same as in Fig. 1.12.

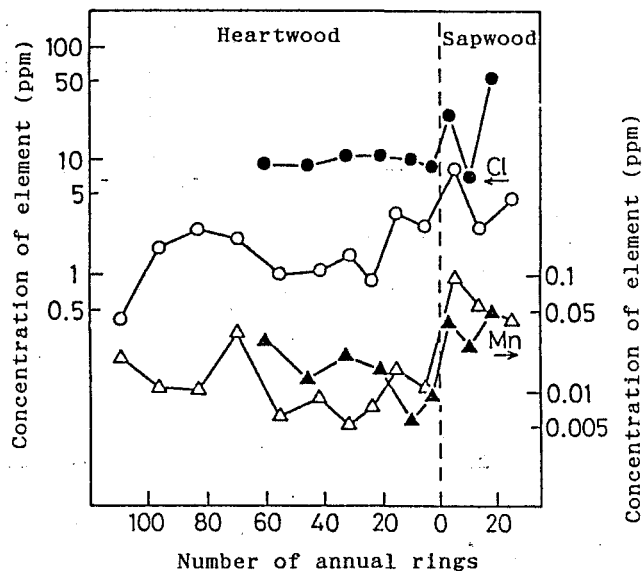


Fig. 1.14 Radial distributions of Mn and Cl in xylem sap at breast height of sugi.
Note: Note is same as in Fig. 1.12.

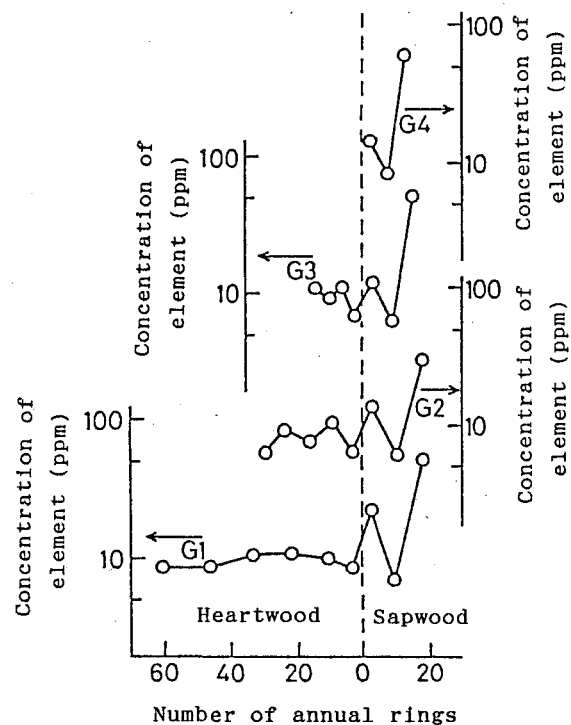


Fig. 1.15 Vertical variation of Cl concentration in xylem sap of Tree G.
Note: G1=1.3 m, G2=4.3 m, G3=7.3 m, G4=10.3 m.

While the concentration of the elements in the xylem sap stayed virtually constant throughout the heartwood, it varied actively in the sapwood. In particular, it showed a sharp rise toward the cambium in the outer sapwood in Tree G. Furthermore, decrease in alkali metals from the outer heartwood to the center of the sapwood was more abrupt in Tree G than in Tree R. On the other hand, the element concentration levels in the heartwood were greater in Tree G than in Tree R. These difference in concentration levels between Trees G and R, at least partly, reflect their respective physiological conditions in May and November.

Average concentrations of K, Mg and Ca in the xylem sap of heartwood at breast height were 2400, 57.5, and 83.4 ppm, respectively in Tree G, and 923, 24.3, and 31.8 ppm in Tree R, respectively. These values were higher, especially in Tree G, than those reported in Bollard's review (1960) in which the average concentrations of those elements in the bleeding sap of corn were 115 ppm (K) and 35 ppm (Ca), and the highest levels in extracted sap of the apple tree were 175 ppm (K) and Mg 20 ppm (Mg). It seems significant that the nutrient elements in the xylem sap were more abundant in the heartwood whose tissue is not alive than in the sapwood. Considering that nature of the above elements are natural-abundant and are cations, they possibly regulate pH as the counter ions of heartwood extractives. The pH value and buffer capacity of sap would be related closely to solubility and mobility of constituents, minerals and extractives, and to the coloration of xylem (Ohashi et al. 1985).

The concentrations of most of the elements were

greater in the inner-most sapwood, i.e. the white zone, than in the center of the sapwood, which is the main pathway of the transpiration stream. The small moisture content of 50 - 80 % in the white zone and the following pit aspiration would prevent the free conduction of water between the heartwood and the sapwood. This might act to maintain the larger concentrations of alkali metals in the heartwood than in the sapwood.

As described above, each element in the xylem sap was distributed similarly in the radial direction at all stem heights. The result of Cl is shown in Fig. 1.15. Bollard (1953) reported that the increase of nutrient elements (N, P, K and Mg) was noticed in the tracheal sap of an apple-tree during flower opening. He presumed that this was attributable to the translocation of the reserves. A similar change was expected with Tree G, but no significant trend could be found between the upper crown part and the lower stem.

(b) Element content in wood substance

The element content in the wood substance probably changed during the heartwood formation, although it was not as abrupt as in the xylem sap (Figs. 1.16 to 1.18). This change would be related to the secondary changes of the tissue such as the deposition of heartwood substance in cell walls. Both between the sapwood and the heartwood, and also between Trees G and R, the difference in concentration of each element was smaller in wood substance than in xylem sap.

The elements in xylem are thought to exist in two states, i.e. dissolved in the xylem sap and fixed in/on the cell walls. In the latter state, they probably are bound to the wall or adsorbed on its surface. Many ele-

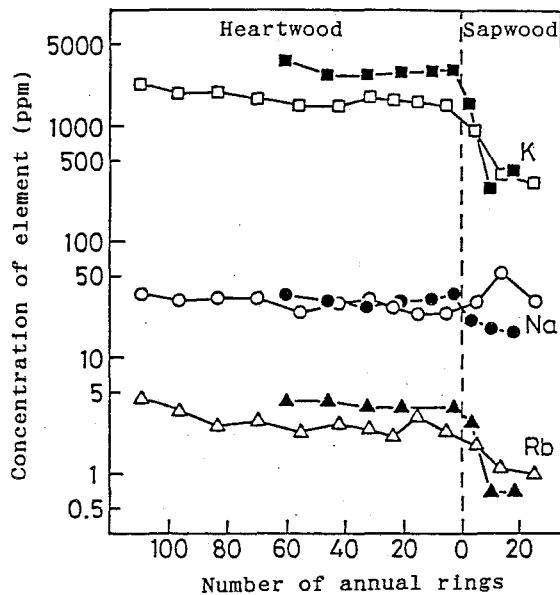


Fig. 1.16 Radial distributions of Na, K and Rb in wood substance at breast height of sugi.

Note: Note is same as in Fig. 1.12.

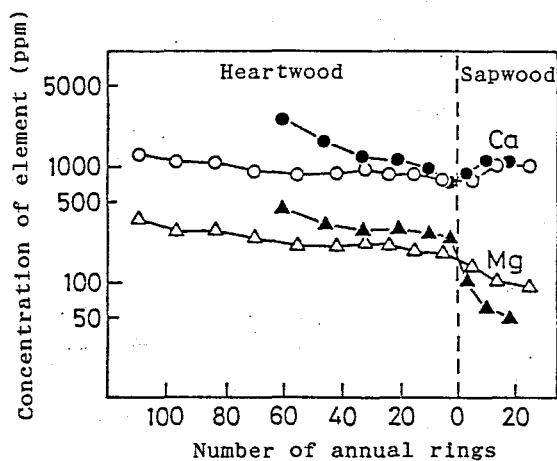


Fig. 1.17 Radial distributions of Mg and Ca in wood substance at breast height of sugi.

Note: Note is same as in Fig. 1.12.

ments may enter cell walls, since the wet cell walls have free spaces which are large enough to allow significantly large size of molecules (Hillis 1977). Fifteen elements are actually detected in the cell walls of black spruce (*Picea mariana* Mill.) (Saka and Goring 1983). Moreover, it has been confirmed that several metal ions and inorganic electrolytes can penetrate cell wall (Sadoh 1986).

The element content in the xylem sap changes easily by responding to changes in the physiological and environmental conditions. In contrast to the sap, the wood substance probably can not exhibit such rapid response, as it is difficult to be translocated. Comparing of the radial pattern in wood substance and that in the xylem sap, change in concentrations of the elements in the xylem sap might occur first, and it would result in the change in the wood substance.

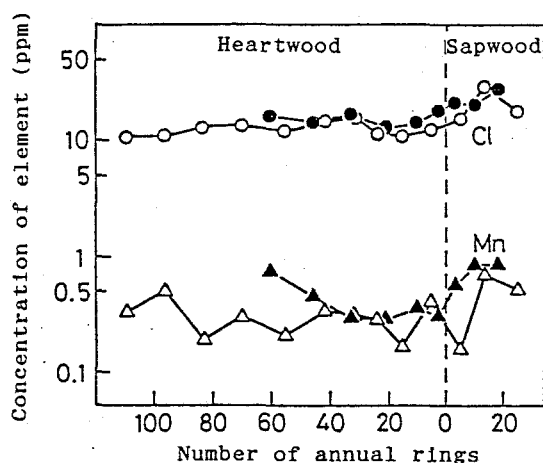


Fig. 1.18 Radial distributions of Mn and Cl in wood substance at breast height of sugi.

Note: Note is same as in Fig. 1.12.

(c) Partition of elements between xylem sap and wood substance

As far as movement of the materials in the xylem sap in the stems of trees, the rate of movement will be governed in part by concentration gradient. In particular, as for ion movement in the heartwood, in which the physiological regulation hardly act, the diffusion and the adsorption on cell wall which processes are largely restricted from the concentration of materials influence the translocation of trace elements. In other words, the greater the difference in element content between the sap and the wood substance, the more easily the element to translocate. Therefore, the partition of each element between the xylem sap and the wood substance is expected to be an indication of its mobility in the stem. To estimate this, concentration ratio of each element in the xylem sap to that in the wood substance was calculated (Table 1.6).

Table 1.6 Concentration ratio (sap/wood substance) of some element in sugi.

Sample	Na	K	Rb	Mg	Ca	Mn	Cl
Tree G							
SW ^{a)}	0.20	0.28	0.24	0.11	0.032	0.054	1.1
HW ^{a)}	1.0	0.81	0.89	0.19	0.064	0.040	0.60
Tree R							
SW	0.09	0.23	0.15	0.10	0.079	0.26	0.30
HW	0.68	0.54	0.52	0.11	0.040	0.045	0.14

Note: The mean for the samples at breast height is shown.

a) SW and HW represent sapwood and heartwood, respectively.

The ratios obviously differed between the sapwood and the heartwood. The values of alkali metals were greater in the heartwood than in the sapwood, whereas those of Mn and Cl were greater in the sapwood. This is attributable to the secondary change in tissue. Parenchyma cells are alive in the sapwood, but they are dead in the heartwood. The transpiration stream ascends only in the sapwood. These must influence the composition and chemical form of elements in each part.

The results in Table 1.6 almost correlate to mobility in the phloem of herbaceous plant (Epstein 1972a). The elements having large values of the ratio (alkali metals and Cl) appeared to be mobile in the xylem, whereas those of small values (Ca and Mn) appeared to be immobile. Magnesium seemed to be intermediate in the xylem, although it was reported as mobile in the phloem (Epstein 1972a). Ions of the mobile elements are mostly univalent cations or anions, whereas those of the immobile elements are mostly larger valent cations. This is consistent with the fact that cell walls are negatively charged. Adsorption on cell walls influences the mobility of ions in the stem.

1.4 Summary

In this chapter, trace elements in the stems of several sugi samples were determined by INAA, and discussed the affecting factor on their radial distributions. Several trace elements occurring in the stem of mature sugi generally showed characteristic distribution pattern for individual elements in radial direction regardless of the tree age and the growing site. Elements with similar chemical properties, such as

alkali metals or halogens, often have similar patterns. Two types of changes in the elemental distributions were observed as the heartwood formed, i.e., increases (Na, K, Rb, Cs and Mg) and decreases (Mn, Cl and Br). This suggests that physiological processes, such as heartwood formation, are main factors that influence trace element distributions in a stem under ordinary growing conditions.

The above patterns for K, Mg, Ca, Mn, and Cl were confirmed in radial distributions of younger trees. The content of K, Mn, and Cl in the sugi disks, even if at different growing stages, varied in patterns similar to the radial distribution at breast height in a mature sugi tree. This was interpreted as the element content in stem tissue changes under the influence of aging.

Therefore, the followings were concluded: 1) translocation of several elements occurs during heartwood formation in the stem of sugi, and 2) the concentrations of some elements (alkali metals and Mg) increase as heartwood formation proceeds, while others (Mn and halogens) decrease. Consequently, the characteristic distribution patterns of elements appear in the radial directions.

The concentration of alkali metals (Na, K, Rb and Cs) and Mg in the xylem sap increased with heartwood formation, whereas Cl and Mn decreased. The concentrations of many elements in the xylem sap rose at the outer sapwood in the growing season. The element content in the wood substance also changed with heartwood formation. The concentration ratio of the xylem sap to the wood substance decreased in order of

Na, K, Rb, Cl > Mg > Ca, Mn.

It appeared to reflect mobility of elements in the stem.

Chapter 2 Distribution of trace elements in stems of softwoods

2.1 Introduction

The distribution patterns of trace elements in the stem of sugi indicated that secondary changes intensively affected translocation of elements in the stem. In particular, many elements in xylem seemed to increase/decrease as heartwood formation proceeded. Therefore, the distribution of the trace elements in the stem is expected to clarify an aspect of the physiological process in stem of trees. In order to investigate the physiological characteristics of tree species, the radial distribution of trace elements in softwood are compared in this chapter.

Before investigating of the trace elements in stem of trees, one must consider what part of the stem is most suitable. First this problem is discussed in this chapter. Then, the distribution of trace elements in stem of major softwoods is mentioned, and physiological property of each species and the difference in behavior of elements are discussed.

2.2 Experimental

2.2.1 Materials

Tokuyama sugi, of which the distributions of trace elements at the breast height were described in chapter 1, was used to investigate the influence of stem position on the trace element distribution. Sample disks were taken every 2 m from the breast height to the top,

and six of them were used for trace element determination (Table 2.1).

For comparison among tree species, eight softwoods were collected (Table 2.2), from which sample disks were taken at the breast height.

Table 2.1 Description of sample disks, Tokuyama sugi.

	Height above ground (m)	Diameter (cm)	Sapwood width (cm)	Number of annual rings	
				Total	Heartwood
T1	1.5	32	4.3	63	45
T4	7.5	21	4.2	29	13
T6	11.5	17	3.2	21	7
T8	15.5	12	2.7	17	-a)
T10	19.5	6.2	3.1	8	-a)
T11	21.5	3	1.5	5	-a)

a) Including no heartwood.

Table 2.2 List of softwood species.

Common name	Scientific name	site	Age
Momi	<u>Abies firma</u>	Ashu ^{a)}	64
Todomatsu	<u>Abies sachalinensis</u>	Furano ^{b)}	134
Karamatsu	<u>Larix leptolepis</u>	Ina ^{c)}	50
Himalayan cedar	<u>Cedrus deodara</u>	Kyoto ^{a)}	30
Akamatsu	<u>Pinus densiflora</u>	Yasu ^{a)}	146
Metasequoia	<u>Metasequoia glyptostroboides</u>	Ashu ^{a)}	19
Sugi	<u>Cryptomeria japonica</u>	Ashu ^{a)}	115
Hinoki	<u>Chamaecyparis obtusa</u>	Yoshino ^{e)}	80

a) Kyoto, b) Hokkaido, c) Nagano, d) Shiga, e) Nara.

2.2.2 Determination of trace elements

Trace elements in the samples were determined by means of instrumental neutron activation analysis (INAA). The preparation of the samples and the procedure of INAA were described in chapter 1.

Some samples contained considerable amount of Mn and/or Al which are easily activated by thermal neutron to yield intensive γ ray. In such case, γ ray prevented measurement of other elements. This is why the atomic absorption spectrometry was applied to some species for determination of K and Mg.

Wood samples (100 - 200 mg dry basis) were dissolved with 2 ml of 6 N HNO_3 at 80 °C, and digested completely at 120 °C. One ml of 1000 ppm Sr solution was added to each sample as a stabilizer, and then the sample solutions were diluted to 20 ml with 0.1 N HCl. Concentrations of elements in the sample solutions were measured with an atomic absorption spectrometer, model Shimadzu AA-640.

2.3 Results and discussion

2.3.1 Vertical variation in distribution of trace elements in a stem

(a) Radial distributions

Concentrations of K and Mn were almost constant in the heartwood region of Tokuyama sugi at any vertical position of the disks (Figs. 2.1 and 2.2). Potassium concentration decreased near the sapwood-heartwood boundary, then reached a minimum at the center of the sapwood, and then increased again toward the cambium. On the other hand, Mn concentration in the sapwood in-

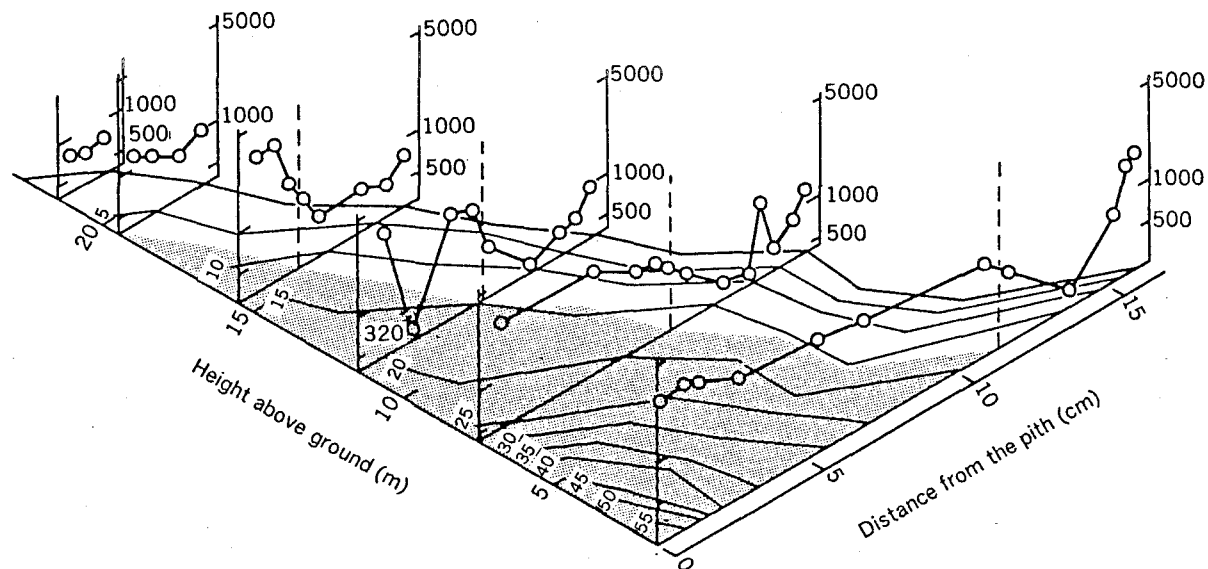


Fig. 2.1 Radial distribution of K at different vertical positions in stem of Tokuyama sugi.

Notes: Dashed lines represent the sapwood-heartwood boundary. The dark area indicates the heartwood region. The axes upright to the illustration represent concentration of the element (ppm).

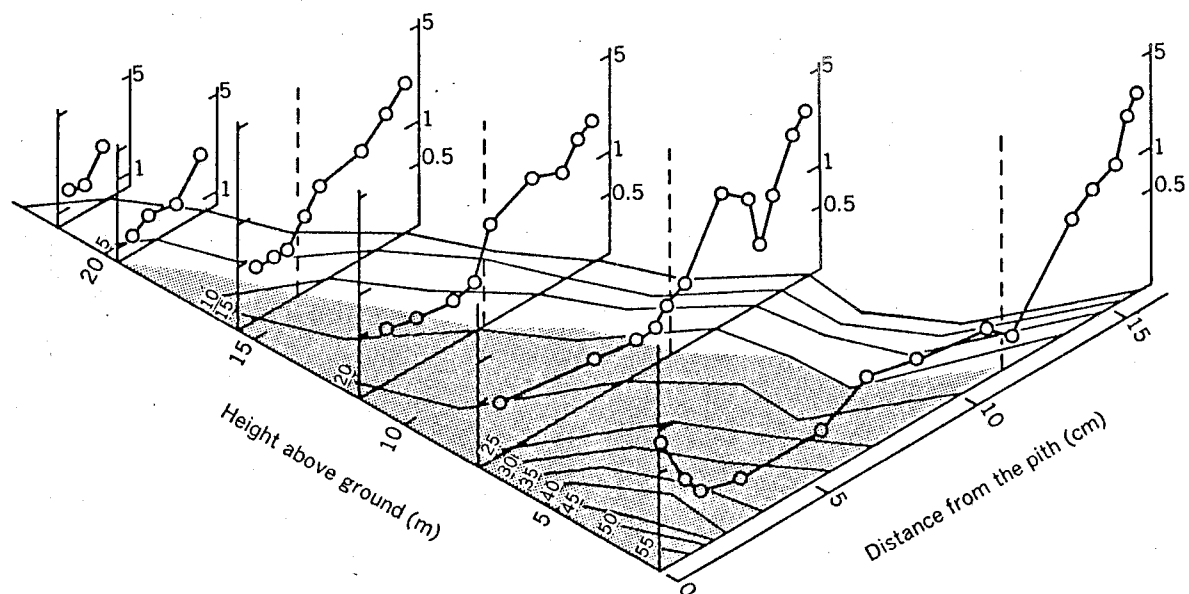


Fig. 2.2 Radial distribution of Mn at different vertical positions in stem of Tokuyama sugi.

Note: Notes are same as in Fig. 2.1.

creased toward the cambium. These distribution patterns are similar to those for the Ashu sugi in chapter 1. Extraordinarily large and small K concentrations were observed at the center of the sapwood in T4 and of the heartwood in T6 compared with the adjacent annual rings (Fig. 2.1). Branch stubs or injuries possibly influence these patterns.

Magnesium and Cl were distributed similarly to K and Mn, respectively. In addition, Ca level was kept essentially constant at any vertical position of the disks as described in chapter 1. The similar trends for K and Ca also have been reported by Furukawa (1964) who surveyed their radial and vertical distributions in stem of sugi. Therefore, the above five elements probably are distributed in their specific patterns in a radial direction at any stem height.

From the standpoint of the period after the stem is formed, the upper part of the stem of a mature tree may correspond to the lower part of the stem of a un-mature one. Therefore, the results shown in Figs. 2.1 and 2.2 would be considered as those in several trees of different ages. The variations in the radial distributions of the elements from the top (T11) to the bottom (T1) were similar to those from the un-matured (Tree A) to the mature tree (Tree F). The radial patterns of Mg and Cl also changed in the same order (T11 to T1). Thus the content of elements at a certain stem height is correlated to number of annual rings. As a result, the characteristic radial pattern described in chapter 1 was found to be common in mature stems.

(b) Variations in a single annual ring

Figures 2.3 and 2.4 show that concentrations of six elements (Na, K, Mg, Ca, Mn and Cl) varied along longitudinal direction in a single annual ring. All samples plotted are outer sapwood.

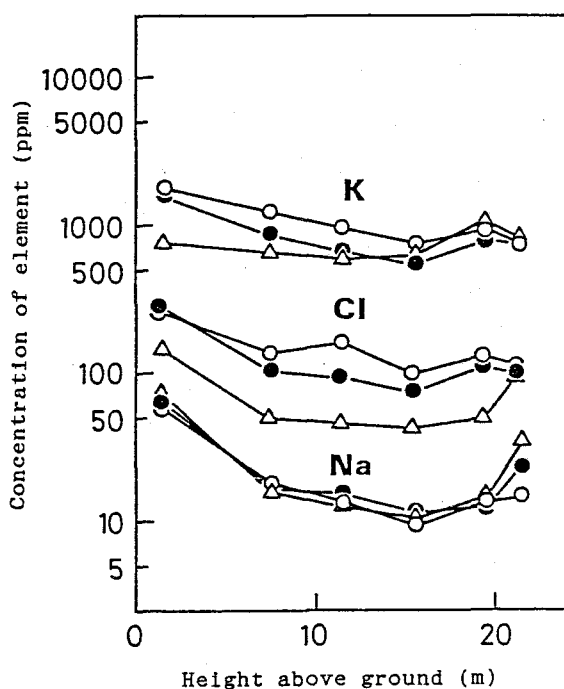


Fig. 2.3 Concentrations of K, Cl and Mn in same annual ring at different vertical positions in stem of Tokuyama sugi.

Notes: ○ : The 1st annual ring from the cambium.
 ● : The 3rd annual ring from the cambium.
 △ : The 6th annual ring from the cambium.

The amounts of all these elements, except Na and Cl, in each annual ring had only small variations at any stem height. Amounts of Na were a few times greater at breast height than at the other positions. A similar trend, not as clear as in the case of Na, was observed for Cl. Furukawa (1964) reported that certain nutrient elements (N, P, K and Ca) varied along longitudinal

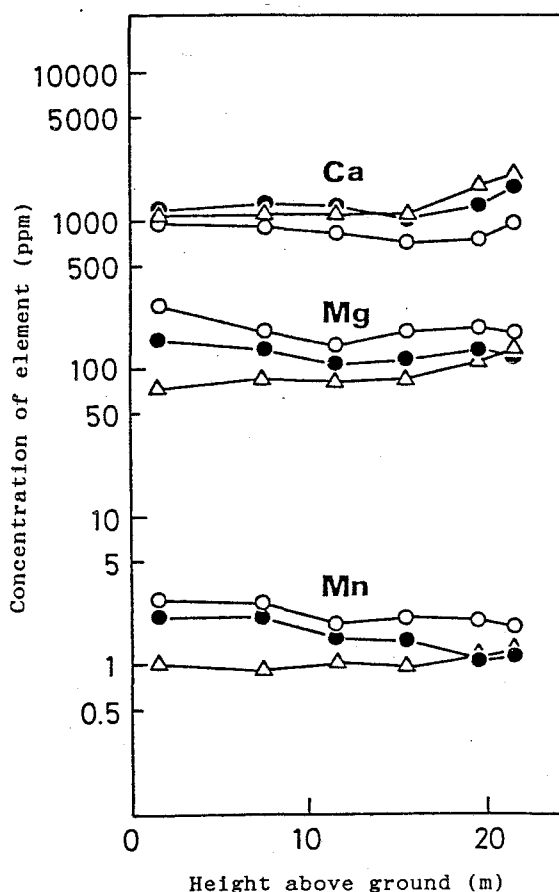


Fig. 2.4 Concentrations of Mg, Ca and Mn in the same annual ring at different vertical positions in stem of Tokuyama sugi.

Note: Notes are same as in Fig. 2.3.

direction with contents at most double in the outermost five annual rings of sugi. Except for near-ground parts, concentrations of these elements were not far different in a single annual ring in the outer sapwood where heartwood had not yet formed.

(c) Vertical variations in the annual rings at the same radial position

As illustrated in Figs. 2.1 and 2.2 (dark area), the heartwood region expands both in the radial and longitudinal directions. The 5th annual ring from the pith already has formed heartwood in the lower stem but still not yet in the upper stem. If heartwood formation affected the element distribution, the distribution pattern observed in the radial direction of the stem would be expected also in the longitudinal direction.

Figures 2.5 and 2.6 show the longitudinal distribution of K and Mn, respectively, at four different radial positions. They have patterns similar to those of each element in the radial section of Tokuyama sugi described in chapter 1. The distributions of Mg and Cl were similar to those of K and Mn, respectively. From these findings, it is certain also that in the longitudinal direction in a stem these elements are redistributed during heartwood formation.

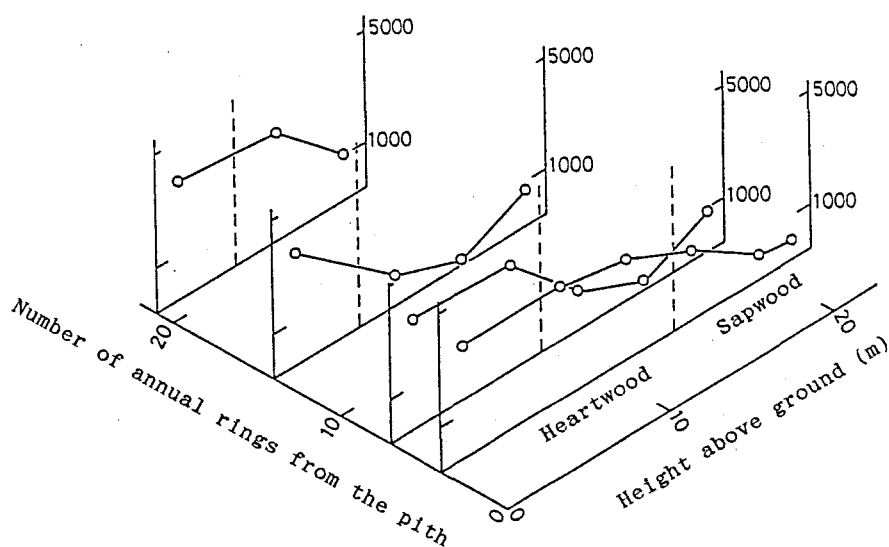


Fig. 2.5 Vertical distribution of K in stem of Tokuyama sugi.

Notes: The axes upright to the longitudinal section of stem represent K concentrations (ppm). Dashed lines indicate the sapwood-heartwood boundary.

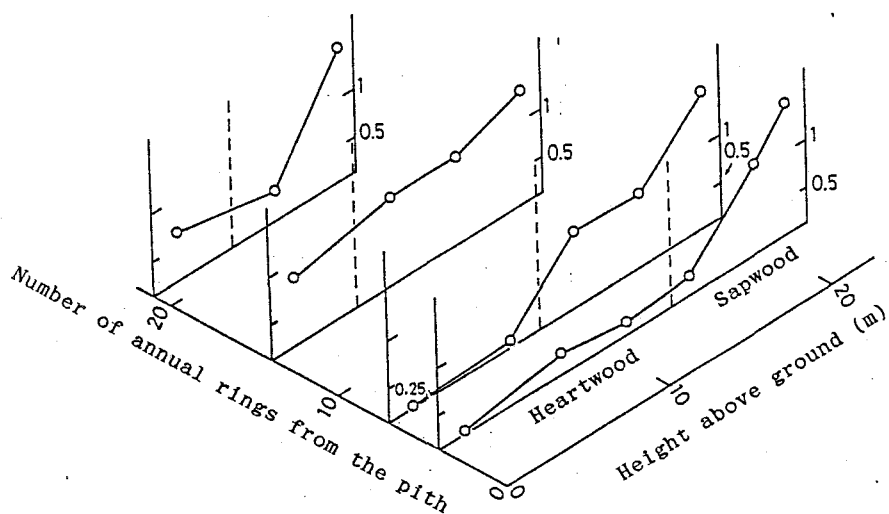


Fig. 2.6 Vertical distribution of Mn in stem of Tokuyama sugi.

Notes: The axes upright to the longitudinal section of stem represent Mn concentrations (ppm). Dashed lines indicate the sapwood-heartwood boundary.

2.3.2 Radial distribution in the stems of softwoods

General profile

Most of the elements surveyed showed a characteristic content change around the sapwood-heartwood boundary. This indicated the redistribution of elements in the stem occurred during heartwood formation, and the process seemed to be specific to elements and tree species.

Although the element content was almost constant in most of the heartwood, it often increased/decreased towards the pith. Galligan et al. (1965) stated that the outward decline in Mn concentration in Douglas-fir (Pseudotsuga menziesii) appeared to correspond with the change from juvenility to maturity. When the reported data for softwood and hardwood species were re-examined, this change in concentration is noticed regardless of tree species (Furukawa 1961, 1964, Tout et al. 1977, Hincman et al. 1978, Brownridge 1984, Taneda et al. 1986).

In the sapwood region, several elements increased at the outermost part, cambium, probably because of high activity of tissue.

(a) Alkali metals

The radial distribution of K in the stems of 6 softwood species are shown in Figs. 2.7 and 2.8. The result for Ashu sugi described in the section 1.3.1 is also shown for comparison.

The characteristic change in K concentration was observed around the sapwood-heartwood boundary: i.e., concentration of K increased in sugi, hinoki (Chamaecyparis abtusa), todomatsu (Abies sachalinensis) and momi (Abies firma) as heartwood formed, whereas it

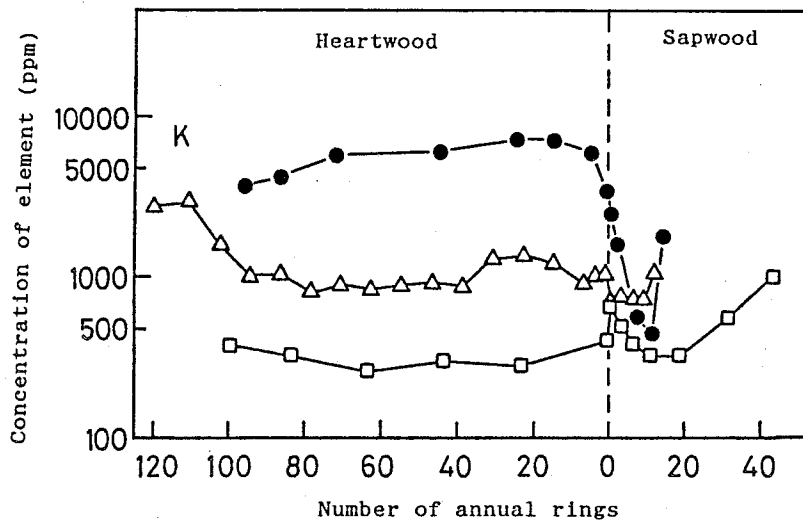


Fig. 2.7 Radial distributions of K in stems of akamatsu, todomatsu and sugi.

Note: □ : akamatsu, △ : todomatsu, ● : sugi.

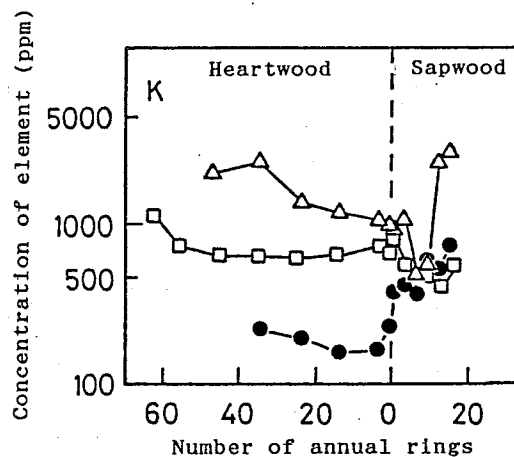


Fig. 2.8 Radial distributions of K in stems of karamatsu, hinoki and momi.

Note: ● : karamatsu, □ : hinoki, △ : momi.

decreased in karamatsu (Larix leptolepis). A small peak at the boundary was observed for akamatsu (Pinus densiflora). High K concentration in the heartwood than in the sapwood was also observed for hinoki (Furukawa 1961, Kohno et al. 1988) and Todomatsu (Fukazawa et al. 1985), and low K concentration for karamatsu (Furukawa 1961, 1966). Potassium content in metasequoia (Metasequoia glyptostroboides) was almost constant from the pith to the cambium. Although content in Himalayan cedar (Cedrus deodara) has not been measured in this study because of the interference of Mn in INAA, Furukawa (1961) has reported a peak around the sapwood-heartwood boundary.

In spite of wide variety among species in K content in the heartwood, the content in the sapwood was not so different. This tendency was observed for other alkali metals detected.

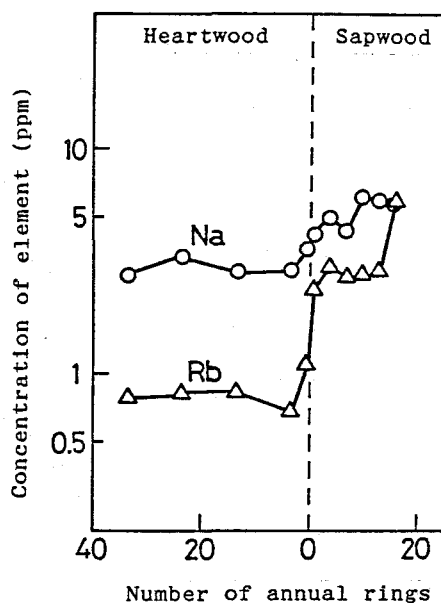


Fig. 2.9 Radial distributions of Na and Rb in stem of karamatsu.

Many of other alkali metals can not have been measured satisfactorily for most of the species, partly because Mn interferes measurement of Na in INAA, and partly because lower content for Rb and Cs. As examples of Na and Rb, their radial distributions in karamatsu is shown in Fig. 2.9. Their radial patterns are similar to that of K, of which trend was described for sugi in chapter 1. This finding is probably noticeable to other species.

(b) Alkaline earth metals

Magnesium in sugi, akamatsu, momi and todomatsu increased during heartwood formation, whereas that in karamatsu and metasequoia decreased (Figs. 2.10 to 2.11). It also increased in the outer sapwood and the pith in most of the species. The radial pattern of Mg is similar to that of K, but variety among the species in content in the heartwood was much narrower than that in K.

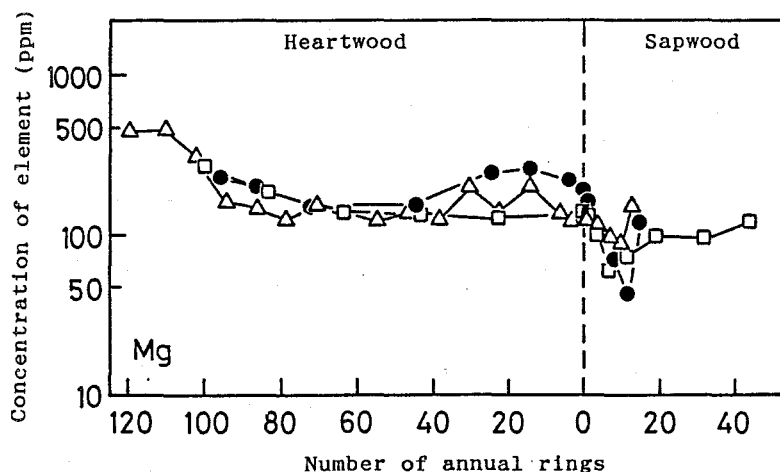


Fig. 2.10 Radial distributions of Mg in stems of akamatsu, todomatsu and sugi.

Note: □ : akamatsu, △ : todomatsu, ● : sugi.

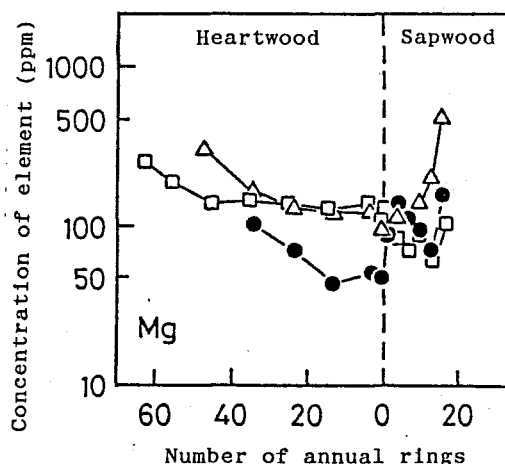


Fig. 2.11 Radial distributions of Mg in stems of karamatsu, hinoki and momi.

Note: ● : karamatsu, □ : hinoki, △ : momi.

Calcium distributed similar to Mg, but its change around the sapwood-heartwood boundary was not so abrupt except karamatsu, metasequoia and Himalayan cedar (Figs. 2.12 to 2.14). Among latter 3 species, Ca decreased rather rapidly during heartwood formation. Calcium is thought to play mainly the structural function as a component of cell wall, and hence to be immobile. However, chemical form of Ca in the stems of those 3 species should be re-examined in future.

Other alkaline earth metals, Sr and Ba, are generally difficult to measure by INAA, and accordingly they were detected only in a few samples. In organism it is known that Sr behaves similarly to Ca, because its ionic radius and ionization potential are very similar to that of Ca. The radial pattern of Sr was usually parallel to that of Ca, whereas Mg was often very different from Ca. Barium content detected in some

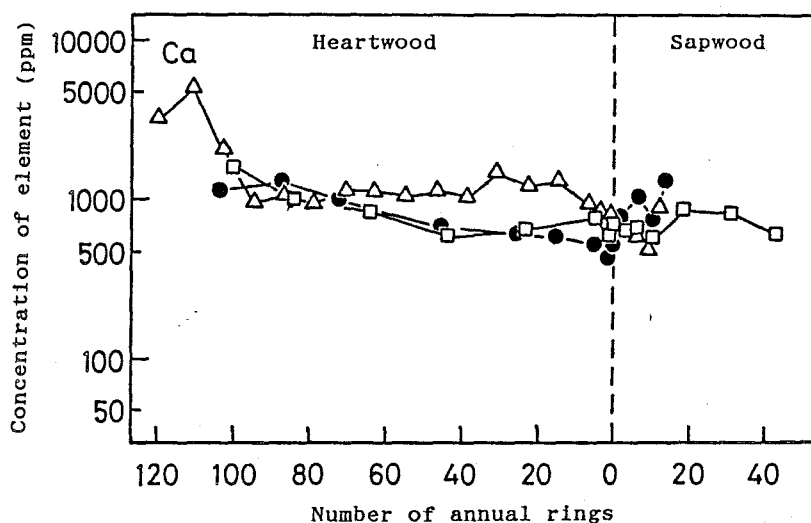


Fig. 2.12 Radial distributions of Ca in stems of akamatsu, todomatsu and sugi.

Note: \square : akamatsu, \triangle : todomatsu, \bullet : sugi.

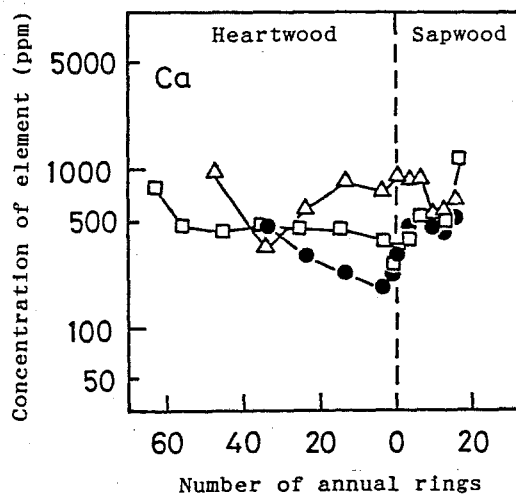


Fig. 2.13 Radial distributions of Ca in stems of karamatsu, hinoki and momi.

Note: \bullet : karamatsu, \square : hinoki, \triangle : momi.

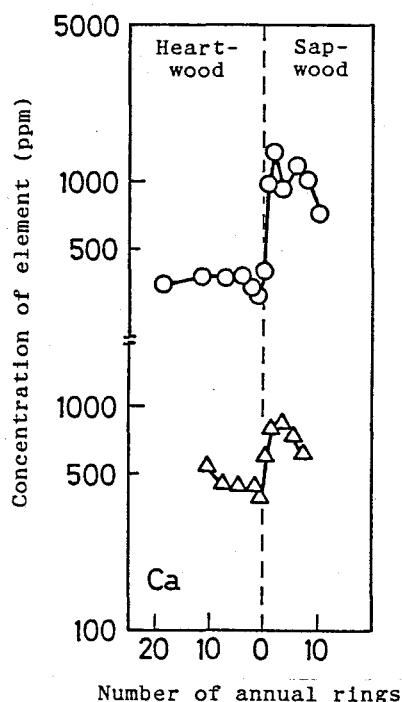


Fig. 2.14 Radial distributions of Ca in stems of Himalayan cedar and metasequoia.

Note: ○ : Himalayan cedar,
△ : metasequoia.

species, in spite of its less abundance in the lithosphere than that of Sr, was sometimes higher (50 - 60 ppm) than that of Sr, but did not show any characteristic change.

(c) Halogens

Chlorine was detected with high accuracy in every species, but Br was in three species, karamatsu, todomatsu and Himalayan cedar (Figs. 2.15 to 2.17). Halogens was, together with alkali metals, one of the element groups of which concentration in the stems was changed greatly from the sapwood-heartwood boundary to the cambium.

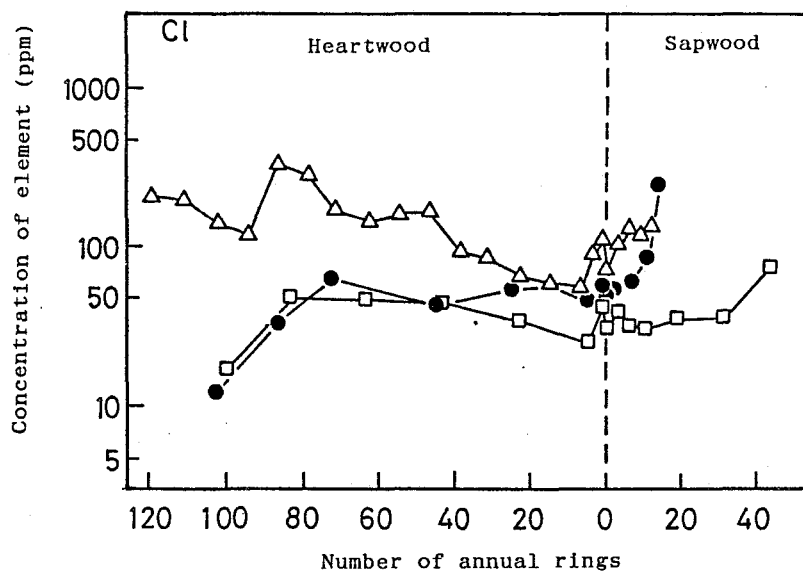


Fig. 2.15 Radial distributions of Cl in stems of akamatsu, todomatsu and sugi.

Note: \square : akamatsu, \triangle : todomatsu, \bullet : sugi.

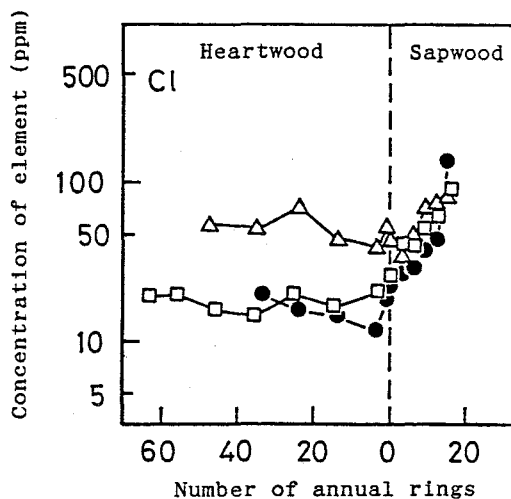


Fig. 2.16 Radial distributions of Cl in stems of karamatsu, hinoki and momi.

Note: \bullet : karamatsu, \square : hinoki, \triangle : momi.

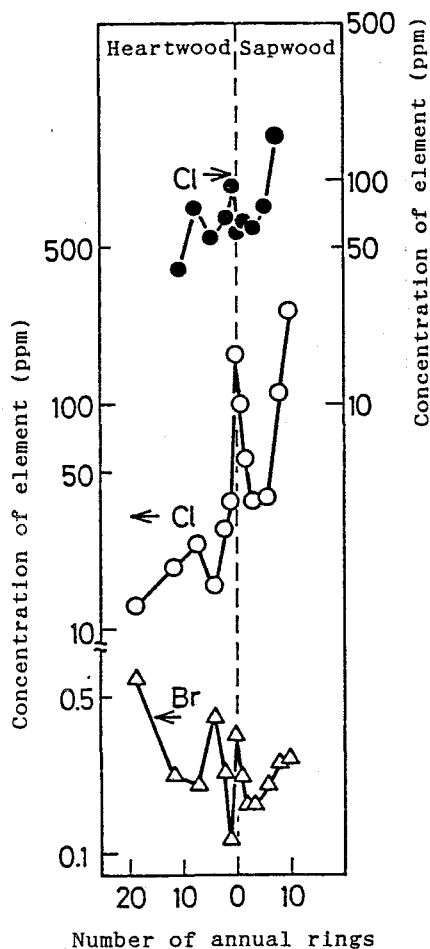


Fig. 2.17 Radial distributions of Cl and Br in stems of Himalayan cedar and metasequoia.

Note: ○, △ : Himalayan cedar,
● : metasequoia.

Chlorine was rich in the outer sapwood in most of the species. It decreased inwards and stayed almost constant in the heartwood except the pith. An extraordinarily high peak was observed at the sapwood-heartwood boundary in Himalayan cedar. A similar peak, not so high as in the Himalayan cedar, was also observed in metasequoia, momi and todomatsu.

The content of halogens and alkali metals in sugi changed reversely each other around the sapwood-heartwood boundary as described in chapter 1: i.e., that is, halogens increased outwards, whereas alkali metals decreased. The radial profiles of halogens and alkali metals in many softwood species surveyed were rather different. However, those in karamatsu changed similarly.

(d) Other metals

Manganese showed a wide variety in its content among the species, and its concentration in a stem often changed remarkably around the sapwood-heartwood boundary (Figs. 2.18 to 2.20). A high peak at the

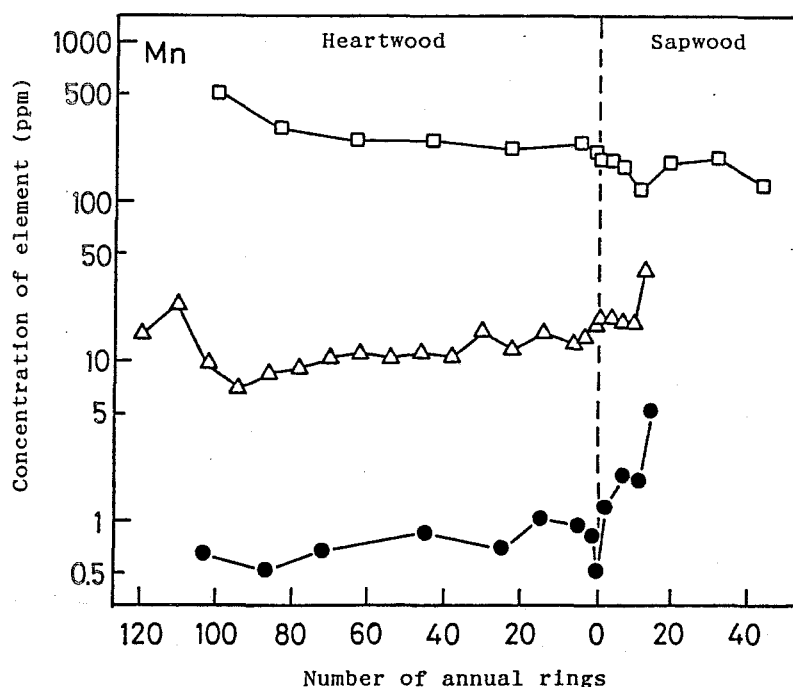


Fig. 2.18 Radial distributions of Mn in stems of akamatsu, todomatsu and sugi.

Note: □ : akamatsu, △ : todomatsu, ● : sugi.

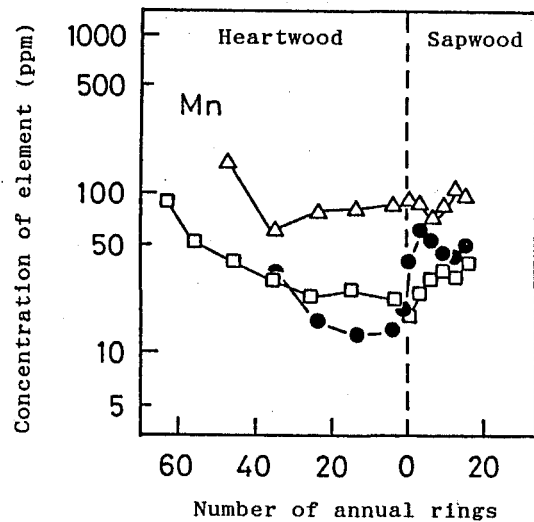


Fig. 2.19 Radial distributions of Mn in stems of karamatsu, hinoki and momi.

Note: ● : karamatsu, □ : hinoki, △ : momi.

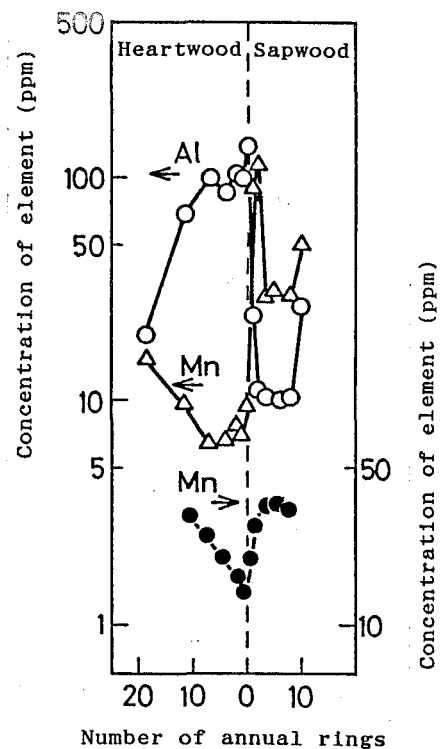


Fig. 2.20 Radial distributions of Mn and Al in stems of Himalayan cedar and metasequoia.

Note: ○ : Himalayan cedar, △ : metasequoia.

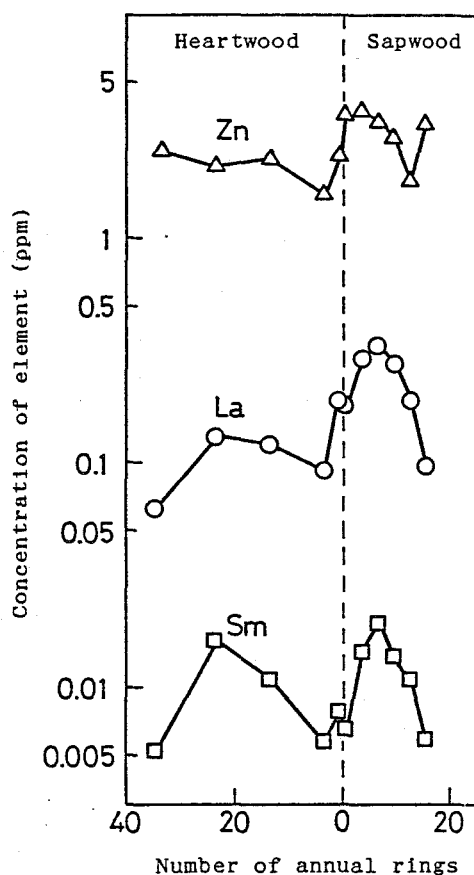


Fig. 2.21 Radial distributions of La, Sm and Zn in stem of karamatsu.

sapwood-heartwood boundary was observed in Himalayan cedar. The same type of pattern was observed for halogens in the same species. Manganese and halogens often showed a similar distribution pattern around the sapwood-heartwood boundary despite of difference in their chemical properties. In such case, their behavior during heartwood formation may have a certain relation.

Aluminum content in Himalayan cedar increased abruptly during heartwood formation and was extraor-

dinarily high in the heartwood. In other species it was less than 10 ppm, and did not show any significant change during heartwood formation. It is interesting to note that Al, not known to be essential to plants, was accumulated in the heartwood of Himalayan cedar.

Two rare earth elements, La and Sm, were detected in the stem of karamatsu (Fig. 2.21). The radial patterns of these elements were parallel and rather different from those of other elements: i.e., they decreased in the pith and outermost sapwood, and had a maximum at the slightly inner part of the sapwood center. In addition, La content in the stem of karamatsu (60 - 330 ppb) was quite high compared with that of leaves of Pinaceae (up to 200 ppb; Koyama et al. 1988), although the leaves are generally richer in element content than the stem. Therefore, this may be suggested that certain physiological processes other than heartwood formation will affect their redistribution, although it is not confirmed whether these elements have a particular role.

2.3.3 Characteristics of element content in softwood species

From the result of previous section, trace elements in the stems of softwood species appeared to be distributed under the influence of physiological factors, especially heartwood formation. In order to compare the redistribution resulted during heartwood formation for each element and tree species, the medians of analytical values were used. In this comparison, it was found that the median was a better value to represent the concentration level of element than the mean.

Some elements increased/decreased abruptly near the pith or the cambium, of which change was not caused not by heartwood formation. Consequently, such extraordinary value would affect more greatly the mean than the median. Therefore, the median was adopted. The median values of the sapwood and the heartwood were compared for 7 elements (Fig. 2.22).

The range of element content among species was wider in the heartwood than in the sapwood. This trend was particularly distinct for K and Na. This is partly because the element content in the sapwood, which contains living tissues, must be kept at a certain level, whereas it is not so in the heartwood. In addition, the inherent nature of secondary metabolism in each species will be reflected more intensively in the heartwood than in the sapwood.

The range of element content for each alkaline earth metal was narrower than those of other elements analyzed, and the trend is slightly different from the result for hardwood species. This will be mentioned in the next chapter. On the other hand, the range of each alkali metal was generally wide. As mentioned in the previous chapter, this difference in behavior was probably attributable to chemical form of each element, i.e., ions or not. For example, halogens, most of which are present as anion in the living matter, give wide concentration ranges.

Manganese concentration, among the softwood species, showed the widest variety in all the elements analyzed. The level of Mn in most stems was higher in the sapwood than in the heartwood.

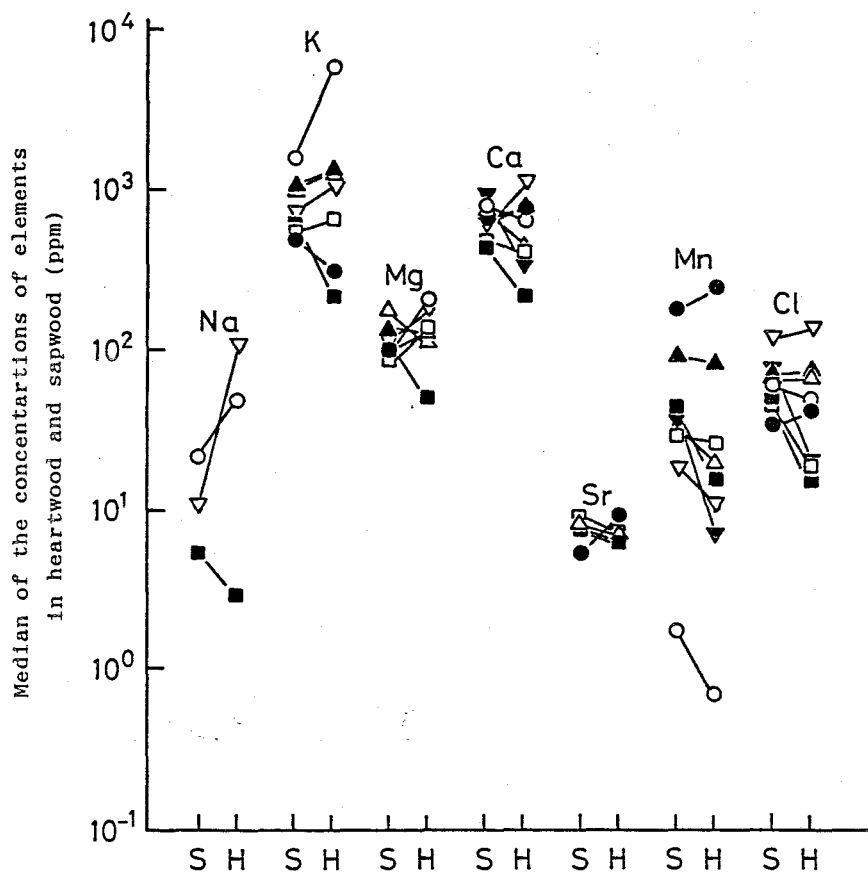


Fig. 2.22 Comparison of element content in sapwood and heartwood among the softwood species.

Notes: S: sapwood, H: heartwood.

○ : Sugi, □ : Hinoki, ▲ : Momi, △ : Metasequia,
 ● : Akamatsu, ▽ : Todomatsu, ■ : Karamatsu,
 ▼ : Himarayan cedar

2.4 Summary

The radial distribution patterns of trace elements were examined at several stem height in the single sugi tree described in the chapter 1. However, the distribution patterns in the longitudinal direction in a stem were similar to those in the radial direction. Element content in stem tissue changes under the influence of aging.

The radial distributions of trace elements in the stems of 8 softwood species changed significantly during the heartwood formation. The radial pattern of element content was classified into 3 types: 1) increasing during the heartwood formation; 2) decreasing during the heartwood formation; 3) showing a peak at the sapwood-heartwood boundary.

The elements of similar chemical properties such as alkali metals or halogens were often distributed similarly in a species. In some species, however, most of the elements detected were distributed similarly in radial direction regardless of their chemical properties.

Alkali metals in softwood species were generally higher in the heartwood than in the sapwood, whereas Mn and Cl were higher in the sapwood. Alkaline earth metals, except Mg, did not show any remarkable change during the heartwood formation.

Chapter 3 Radial distributions of trace elements in stem of hardwoods

3.1 Introduction

The radial distributions of trace elements in the stems of softwoods showed the characteristics in their inherent nature of mineral metabolism. In particular, the elements in a stem seemed to be distributed in a species- or genus-specific pattern which is closely related to the heartwood formation.

Following the study on softwood species, to investigate movement and accumulation of trace elements in stems of hardwoods, 21 hardwood stems are surveyed in this chapter. Prior to the comparing among the hardwood species, the result for mizunara (Quercus mongolica var. grosseserrata) was examined what parts of the stem is suitable for this purpose.

One of author's concerns is to find a relationship between trace elements and physiological process, in particular, how the distributions of trace elements reflect characteristic of heartwood formation in each species. And another concern is to grasp natural background in order to evaluate net human impacts on the environment.

3.2 Experimental

3.2.1 Samples

A mizunara tree to examine the influence of stem position on element distribution pattern was harvested in the Ashu Experimental Forest, Kyoto University, (Kyoto Prefecture) in September, 1983. Disks were taken

every 2m from breast height, and four of them were used (Table 3.1).

Table 3.1 Description of sample disks.

Sample disks	Heights (m)	Diameters (cm)	Annual rings
M1	1.2	33	75
M3	5.2	25	61
M5	9.2	17	46
M7	13.2	9	33

Note: Tree height was 18.3 m.

Table 3.2 List of hardwood species.

Common name (Scientific name)	Site	Age
Yurinoki (<u>Liriodendron tulipifera</u>)	b	65
Hoonoki (<u>Magnolia obovata</u>)	a	48
Kanakuginoki (<u>Lindera erythrocarpa</u>)	a	81
Natsutsubaki (<u>Stewartia pseudo-camellia</u>)	a	250
Azukinashi (<u>Sorbus alnifolia</u>)	a	102
Nanakamado (<u>Sorbus commixta</u>)	a	65
Kihada (<u>Phellodendron amurense</u>)	a	36
kohauchiwakaede (<u>Acer sieboldianum</u>)	a	154
Kenponashi (<u>Hovenia dulcis</u>)	a	40
Mizuki (<u>Cornus controversa</u>)	a	45
Harigiri (<u>Kalopanax pictus</u>)	a	73
Koshiabura (<u>Acanthopanax sciadophylloides</u>)	a	60
Keyaki (<u>Zelkova serrata</u>)	a	79
Enoki (<u>Celtis sinensis</u>)	b	40
Mizume (<u>Betula grossa</u>)	a	221
Buna (<u>Fagus crenata</u>)	a	105
Konara (<u>Quercus serrata</u>)	a	60
Mizunara (<u>Quercus mongolica</u> var. <u>grosseserrata</u>)	a	75
Kuri (<u>Castanea crenata</u>)	a	57
Hakuunboku (<u>Styrax obassia</u>)	a	88
Tochinoki (<u>Aesculus turbinata</u>)	a	64

a: Ashu Experimental Forest, Kyoto University.

b: Botanical Garden, Kyoto University.

Twenty one hardwood species were collected mainly from the Ashu Experimental Forest and some from the Botanical Garden, Kyoto University (Table 3.2). Sample disks were taken at breast height or under crown height when it was impossible.

3.2.2 Determination of trace elements

Instrumental neutron activation analysis (INAA) was applied to determine concentration of elements. Atomic absorption spectrometry (AAS) was also applied to a few species. The preparation of samples and the procedures of INAA and AAS were described in chapters 1 and 2.

3.3 Results and discussion

3.3.1 Radial distributions of elements at different stem height

In describing the radial distributions of elements in stems of trees, one must consider what part of stems are the most typical. In chapter 2, the influence of vertical position on the distributions of elements in sugi was discussed prior to comparison among the softwood species. This also is first considered in this chapter.

Figure 3.1 shows the radial distributions of Na at 4 different vertical positions. The sapwood-heartwood boundary was determined by dark coloration of the xylem, and consequently, it might be slightly different from the actual boundaries. The shift of the peak in disk M7 was attributed to this.

The radial patterns of Na at various stem height

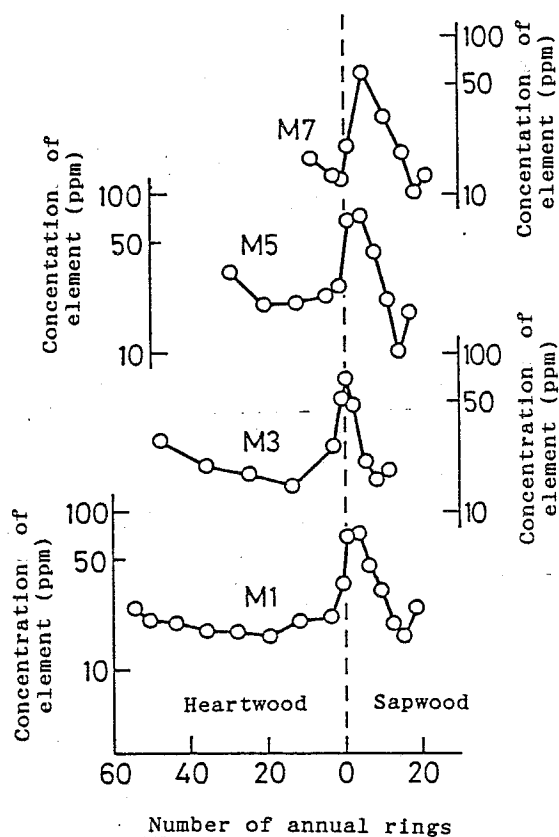


Fig. 3.1 Radial distributions of Na at different vertical positions in stem of mizunara.

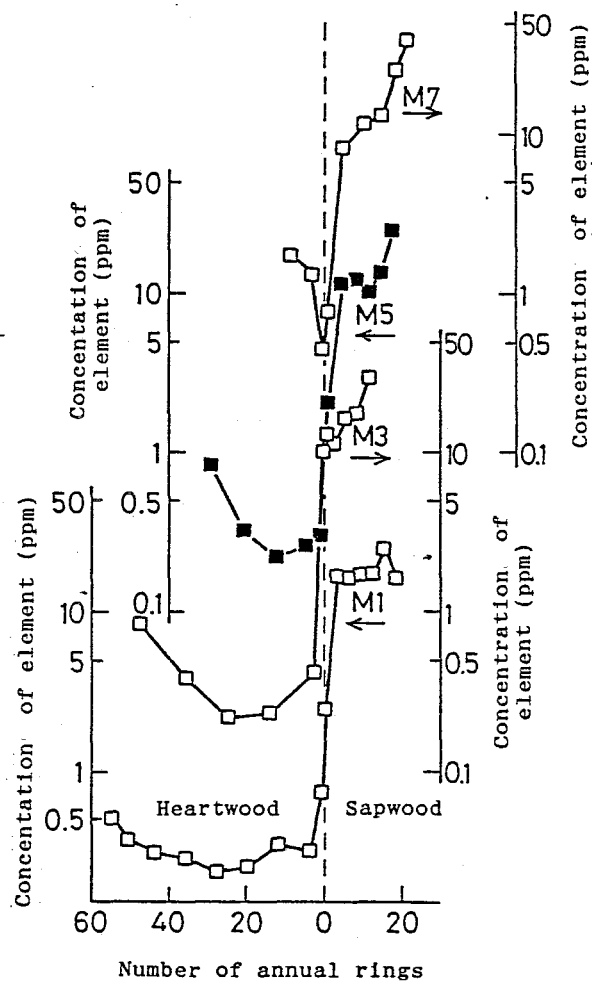


Fig. 3.2 Radial distributions of Mn at different vertical positions in stem of mizunara.

were all nearly the same, except the uppermost disk had less heartwood than the lower ones. This also is true in the distributions of Mn (Fig. 3.2). The concentrations of these 2 elements showed the characteristic change particularly near the sapwood-heartwood boundaries.

Increases near the pith and the outer sapwood also were observed. The former increase probably was related to the constituting xylem elements in their growing stages, and the latter to the cambial zone. In addition, the outer sapwood or differentiating zone in the xylem will transport minerals, which also may contribute to the large element content.

From the results of Na and Mn, one can conclude that data at breast height are the most suitable to be used to compare the radial distribution of each element.

3.3.2 Radial distribution of elements in xylem of hardwoods

(a) Alkali metals

In most species the radial distribution pattern of alkali metals in a stem were generally parallel each other. The element content was changed characteristically around the sapwood-heartwood boundary. The patterns were classified into 3 types mentioned in chapter 2.

Sodium and Rb in natsutsubaki (Stewartia pseud-camellia) increased outwards from the sapwood-heartwood boundary (Type 1, Fig. 3.3). Alkali metals in kihada (Phellodendron amurense) also changed in similar manner

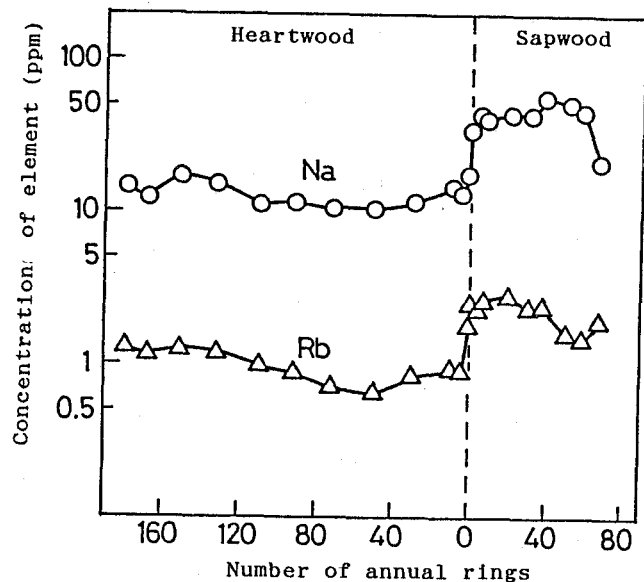


Fig. 3.3 Radial distributions of Na and Rb in stem of natsutsubaki.

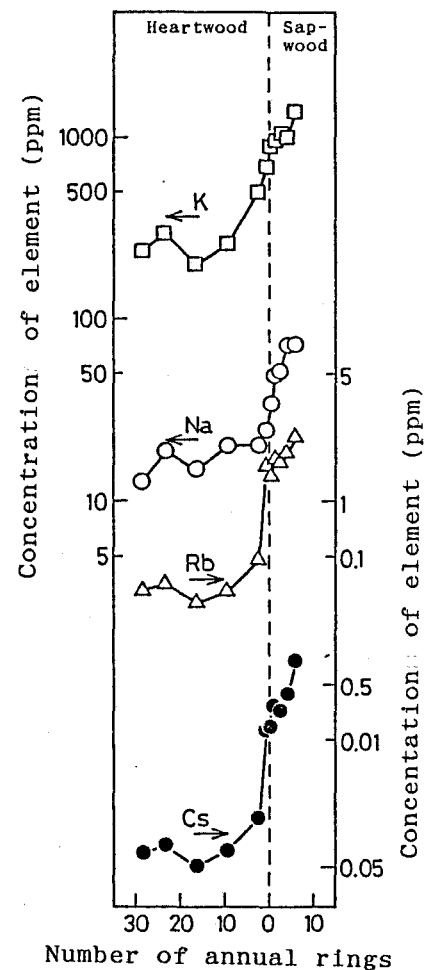


Fig. 3.4 Radial distributions of alkali metals in stem of kihada.

to those of natsutsubaki, but their increases were more abrupt (Fig. 3.4). Type 1 included following species: konara (K and Rb; Quercus serrata), keyaki (Zelkova serrata), koshiabura (K; Acanthopanax sciadophylloides), hoonoki (Magnolia obovata) and yurinoki (Liriodendron tulipifera).

There were few species in which alkali metals decreased outwards from the sapwood-heartwood boundary (Type 2). However, pattern of K in azukinashi (Sorbus alnifolia) changed slightly from this manner (Fig. 3.5). Azukinashi is known to have a wide white zone

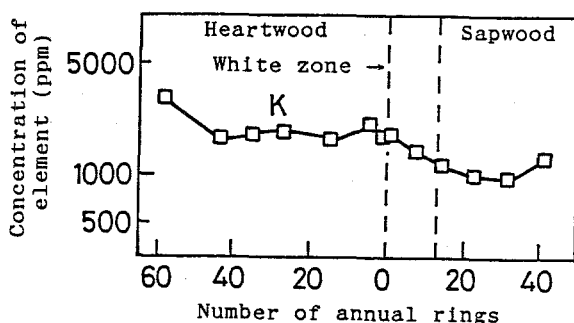


Fig. 3.5 Radial distributions of K in stem of azukinashi.

(Yazawa and Ishida 1965). The figure indicated that the change in K content already occurred in this zone. The similar change in Na content was observed for nanakamado (Sorbus commixta) which is also observed in Sorbus spp. and has a wide white zone.

Each of alkali metals, except Cs, in kenponashi (Hovenia tomentella) had a peak at the sapwood-heartwood boundary (Type 3, Fig. 3.6). The similar peaks were observed also in mizunara (Fig. 3.7). The

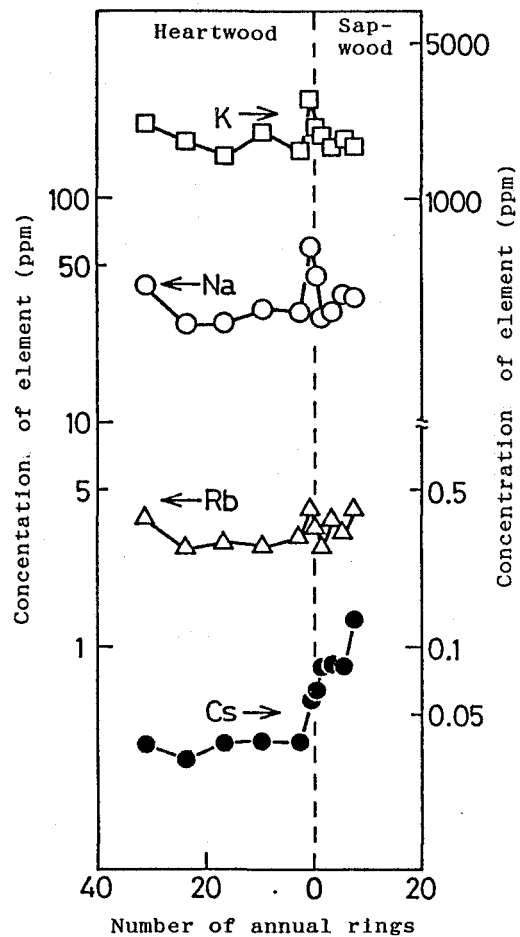


Fig. 3.6 Radial distributions of alkali metals in stem of kenponashi.

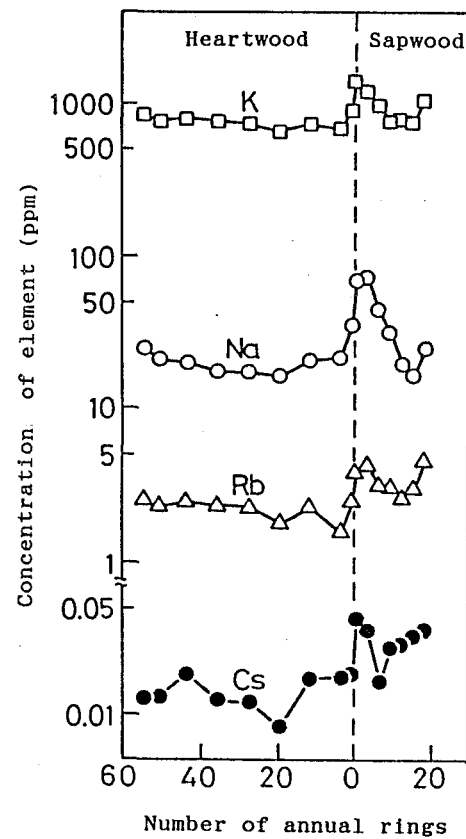


Fig. 3.7 Radial distributions of alkali metals in stem of mizunara.

peaks in mizume (Betula grossa) were rather broad compared with those in the former species (Fig. 3.8). Its large number of sapwood rings and small growth rate possibly related to the rate in mizunara of heartwood formation.

Type 3 of pattern was observed also for kuri (Castanea crenata) and konara (Na). Three species in Fagaceae, kuri, konara and mizunara, were included in this type, and this indicates that they are taxonomically intimate.

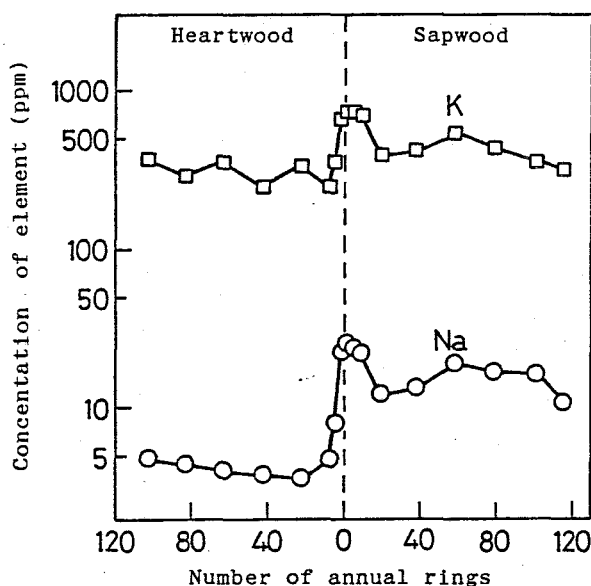


Fig. 3.8 Radial distributions of Na and K in stem of mizume.

Alkali metals in kohauchiwakaede (Acer sieboldianum) did not show significant changes at the sapwood-heartwood boundary. The difference in their content were little between the sapwood and the heartwood. In the species that has a pale heartwood, such as buna (Fagus crenata), hakuunboku (Styrax abassia) and mizuki (Cornus controversa), alkali metal content did not show significant changes. The secondary changes in tissue, especially variety and amount of heartwood substances probably had a close relationship to the distributions of trace elements.

(b) Alkaline earth metals

Except Mg the changes in alkaline earth metal content at the sapwood-heartwood boundary were not so much as those of alkali metals. Magnesium in some species was different from other alkaline earth metals, not only in the radial distribution pattern but also the range of content in a stem. Three types of radial patterns of elements mentioned in chapter 2 was also observed.

Alkaline earth metals in keyaki increased outwards from the sapwood-heartwood boundary (Type 1; Fig. 3.9). This type of pattern also was observed for kuri, konara and mizunara, all of which are in Fagaceae, but increase of Mg at the sapwood-heartwood boundary was more abruptly (Fig. 3.10). In addition, mizume, yurinoki, hoonoki and kanakuginoki (Lindera erthrocarpa) were classified into Type 1. In these 4 species, Mg in hoonoki increased more than 10 times from the heartwood to the sapwood.

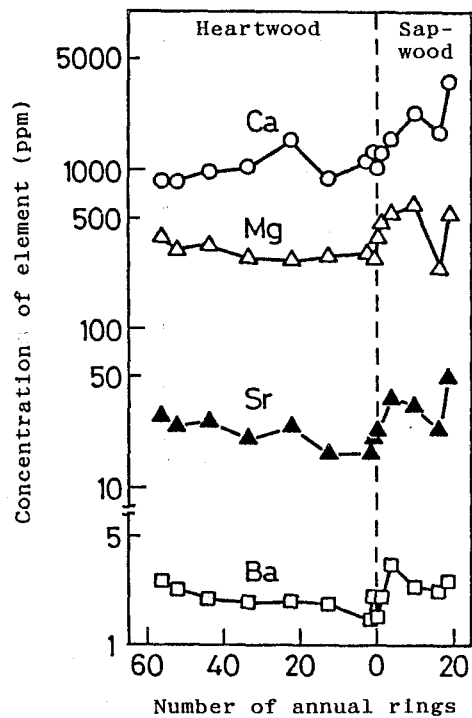


Fig. 3.9 Radial distributions of alkaline earth metals in stem of keyaki.

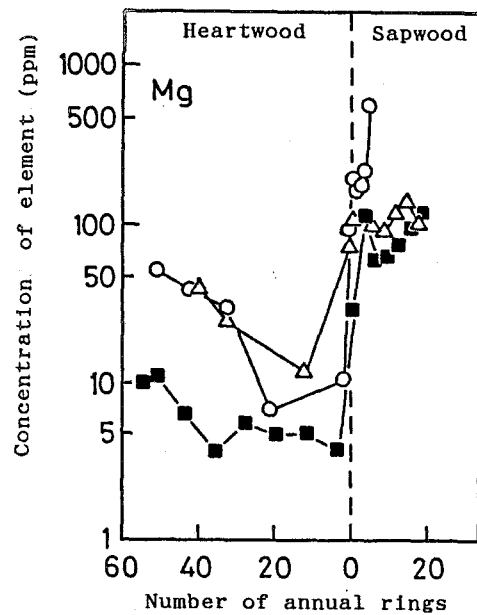


Fig. 3.10 Radial distributions of Mg in stems of Fagaceae.
Note: ○ : Kuri, △ : Konara, ■ : Mizunara.

In several species, content of alkaline earth metal decreased outwards from the sapwood-heartwood boundary (Type 2). This pattern was seldom observed in alkali metals. The radial distributions of alkaline earth metals in azukinashi was shown in Fig. 3.11, in which the elements other than Mg increased as the heartwood formed. It is noteworthy that azukinashi was the only species that belonged to Type 2 in alkali metals (K). Following species were included in Type 2: natsutsubaki, harigiri (*Kalopanax pictus*), koshiabura and kenponashi (Ca).

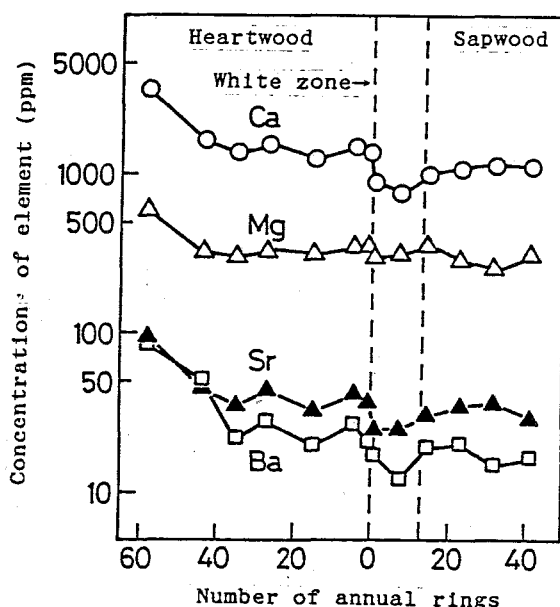


Fig. 3.11 Radial distributions of alkaline earth metals in stem of azukinashi.

Contrary to alkali metals, some species showed a peak at the sapwood-heartwood boundary in their distribution of alkaline earth metals (Type 3). Figure 3.12 showed the distributions in kihada. Only Ca was almost constant at the sapwood-heartwood boundary. Magnesium in kenponashi was also classified into Type 3.

Alkaline earth metals in kohautiwakaede were almost constant through radial direction and did not show a significant tendency even at the sapwood-heartwood boundary (Fig. 3.13). This species has a wide sapwood region and a large number of sapwood rings, and, consequently, the heartwood expands very slowly. This property possibly affects the gradual change in element content. Nobuchi et al. (1987) stated that the distance from the cambium to the sapwood-heartwood boundary is a stronger factor in controlling heartwood formation than the sapwood rings.

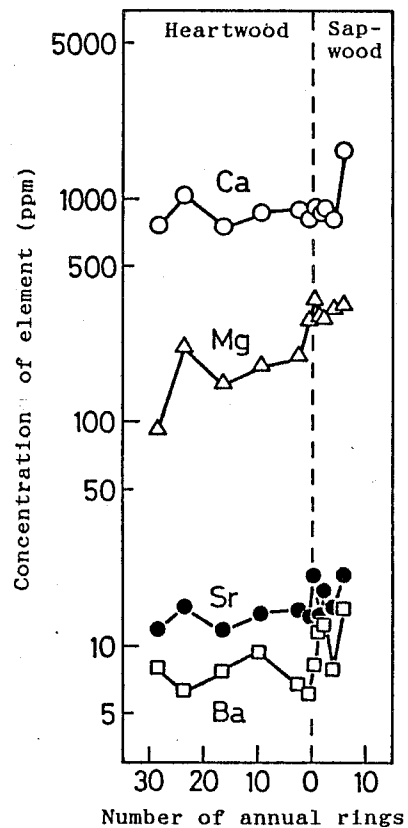


Fig. 3.12 Radial distributions of alkaline earth metals in stem of kihada.

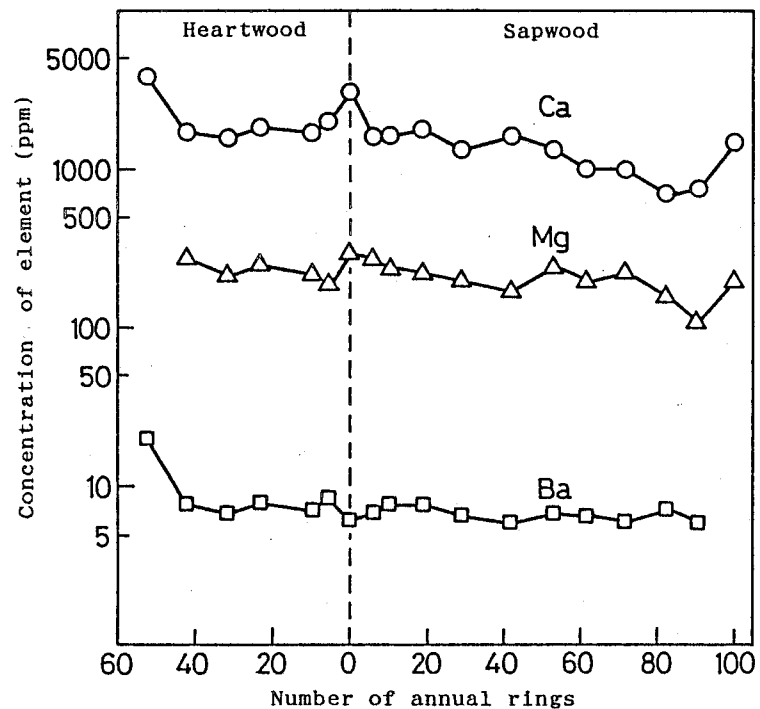


Fig. 3.13 Radial distributions of alkaline earth metals in stem of kohauchiwakaede

(c) Halogens

Among three types of radial pattern of elements, Type 2 was not observed for halogens in hardwood species surveyed. The radial patterns of Cl and Br were often parallel, but the range of the Cl concentration in a stem was wider than that of the Br's.

The radial distributions of Cl and Br in mizunara and keyaki are shown in Figs. 3.14 and 3.15, respectively. The patterns of these elements in mizunara were classified into Type 1. The pattern of Br in keyaki were classified into Type 1, whereas that of Cl was intermediate between Types 1 and 3. The peak at the sapwood center in keyaki probably is not related to the physiological changes in the tissue but to the constituting xylem elements in that part where the ring width were extraordinarily narrow. Type 1 included konara, hoonoki and yurinoki (Cl).

The following species were classified into Type 3: kanakuginoki, kuri, kenponashi and kihada. The distributions in kanakuginoki were shown in Fig. 3.16. The concentrations of Cl and Br in the xylem of kanakuginoki were the largest among the species surveyed. The value in xylem was almost comparable to that of leaves in which element content is much larger than that in xylem. Since concentrations of Cl and Br in leaves of kanakuginoki were not necessarily high compared with those of other species, these 2 elements were thought to be accumulated in xylem. It reflects a difference in physiological properties between xylem and leaves.

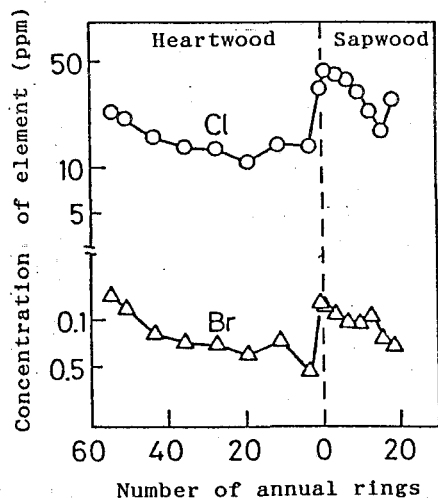


Fig. 3.14 Radial distributions of Cl and Br in stem of mizunara.

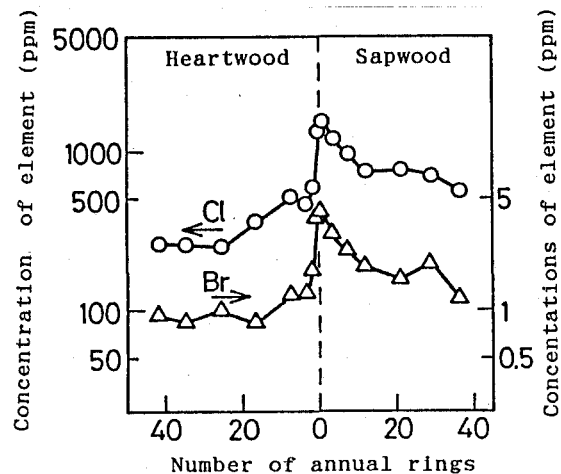


Fig. 3.16 Radial distributions of Cl and Br in stem of kanakuginoki.

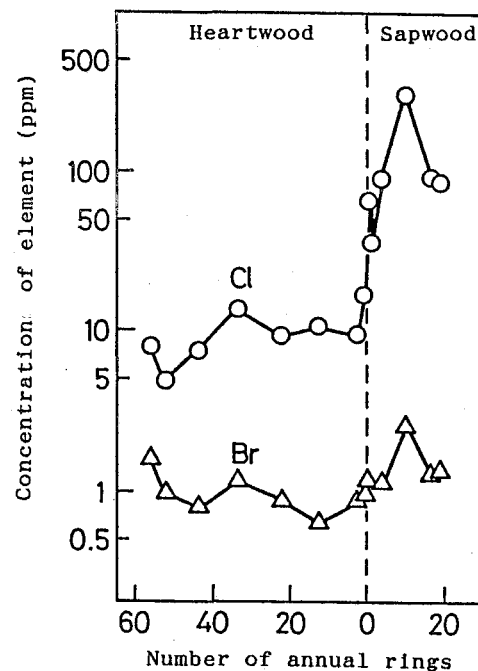


Fig. 3.15 Radial distributions of Cl and Br in stem of keyaki.

(d) Other metals

Manganese and aluminum were detected in all the species surveyed. Zinc was detected in many species and Cu in some species. Rare earth elements (La, Sm and Ce) were detected in some species, and Co and V were seldom detected.

The radial distributions of Al, Mn, Zn and Ce in natsutsubaki are shown in Fig. 3.17. The species in Theaceae, into which natsutsubaki is classified, are known to accumulate Al. Accordingly the Al content in natsutsubaki was much higher than that of other species surveyed. Aluminum in natsutsubaki was distributed parallel to Mn, whereas it was, in most species, distributed randomly in radial direction and was low in content (less than 10 ppm). Aluminum, Mn and Zn increased as heartwood formed and were rich in the heartwood. This type of radial pattern were few in hardwood.

Figures 3.18 and 3.19 show the distributions of Mn, Al and rare earth elements in kihada and kuri, respectively. As seen in Fig. 3.19, rare earth elements were distributed parallel to each other, but this was not true in other metal elements. Aluminum in these figures and Fig. 3.20 in mizunara were distributed in different manner from heavy metals. Its radial pattern were often random and did not indicate any significant trend in many species. Aluminum, an amphoteric metals, is strongly affected its chemical form by pH value of the tissue. Its different chemical properties from other transition elements probably was one of the reasons why its radial distribution did not have common pattern with other elements and among the species.

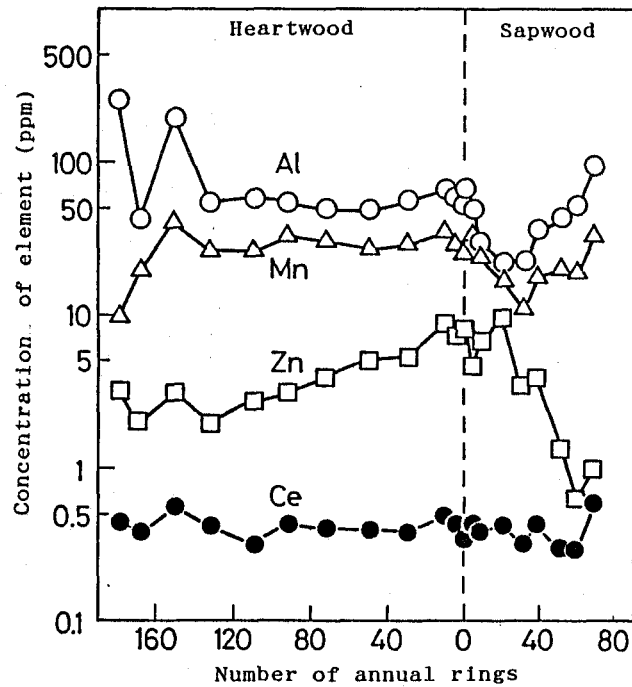


Fig. 3.17 Radial distributions of Al, Mn, Zn and Ce in stem of natsutsubaki.

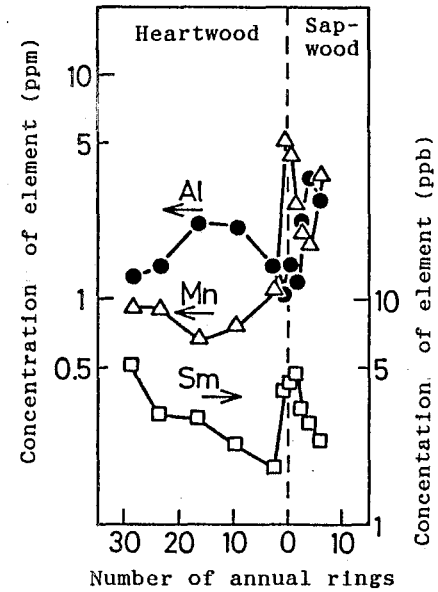


Fig. 3.18 Radial distributions of Al, Mn and Sm in stem of kihada.

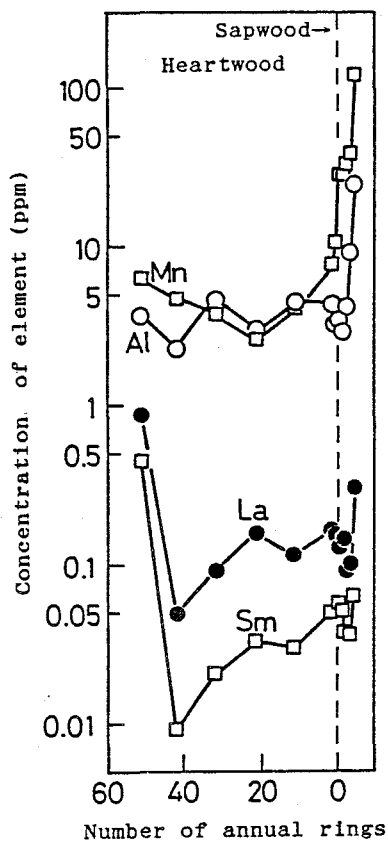


Fig. 3.19 Radial distributions of Al, Mn, La and Sm in stem of *kuri*.

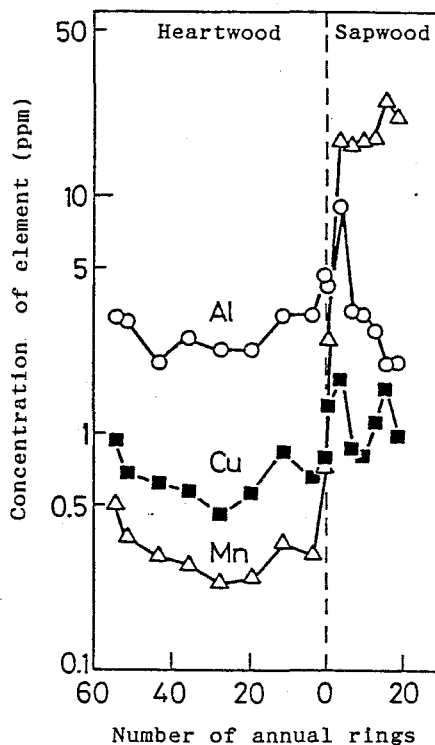


Fig. 3.20 Radial distributions of Al, Cu and Mn in stem of *mizunara*.

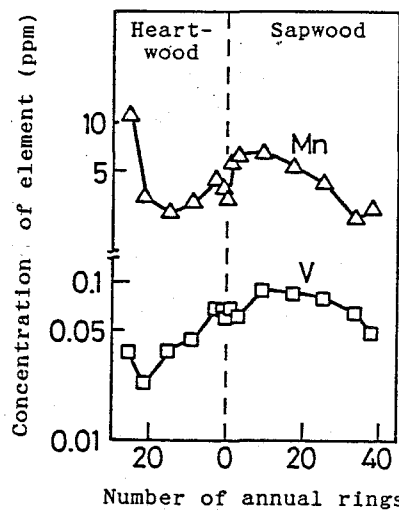


Fig. 3.21 Radial distributions of Mn and V in stem of *yurinoki*.

Vanadium was sometimes detected in a few species. The radial distribution in yurinoki is shown in Fig. 3.21. The distribution curve of V was almost parallel to that of Mn and was higher in its content in the sapwood.

The distributions of metal elements in a stem seemed to depend considerably on their chemical properties, though this is not applicable to all tree species. The difference in distributions of elements were particularly noticeable at the sapwood-heartwood boundary. This indicates, in other words, the physiological influence, especially secondary changes represented heartwood formation.

3.3.3 Characteristics of element content in hardwood species

In order to estimate the redistribution of element during heartwood formation, medians of the concentrations of 6 elements in the sapwood and the heartwood, respectively, were compared for various hardwood species (Fig. 3.22).

The variation of element content among the softwood species was wider in the heartwood than in the sapwood as mentioned in the previous chapter. This tendency was also found in the hardwood species, and, as the case in softwood species, was probably the reflection of the variety of the secondary metabolism in each species.

The ranges of alkali metals in the heartwood of hardwood species were narrower than those of softwood species, whereas the ranges of alkaline earth metals, especially of Mg, in the heartwood were much wider than

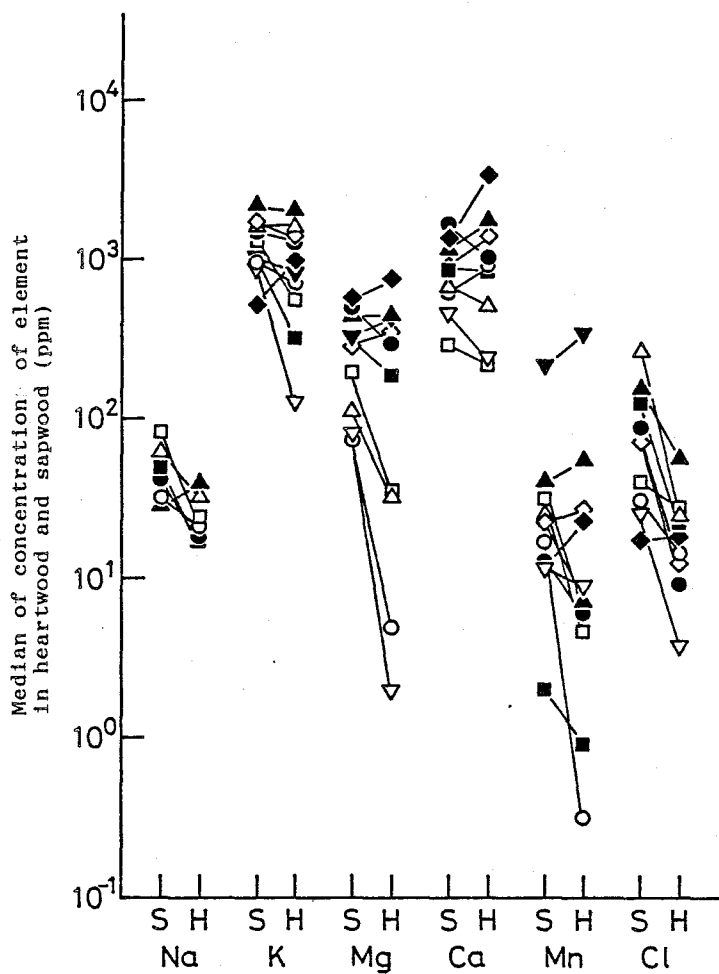


Fig. 3.22 Comparison of element content in sapwood and heartwood among hardwood species.

Notes: S=Sapwood, H=Heartwood.

○ : Mizunara, △ : Knara, □ : Kuri, ▽ : Hoonoki,
◇ : Harigiri, ● : Keyaki, ▲ : Kenponashi, ■ : Kihada,
▼ : Kosiabura, ◆ : Tochinoki.

that of softwood species. Extremely low Mg content in the heartwood was observed for Quercus spp., Castanea spp. and Magnolia spp., and such large concentration difference between the sapwood and the heartwood was not observed in softwood species. This indicates that Mg was redistributed during heartwood formation in those species. In many case, element content in hardwood species was larger in the sapwood than in the heartwood.

Magnesium content in hardwood species was widely distributed among the elements surveyed, and this was also noticed in softwood species. The range of Mn content in a stem, especially in Quercus spp., abruptly increased from the heartwood toward the sapwood, of which increase was little observed in softwood species. Although Mn in the sugi stem appeared to be less mobile as mentioned in chapter 2, this was not always true in hardwood species. Memon and Yatazawa (1982) reported that very little Mn was tightly bonded to cellulose or lignin of the leaf tissue of three accumulator plants in Araliaceae.

Chlorine content in hardwoods was larger in sapwood than in heartwood. This trend was commonly noticed both in softwoods and heartwoods, but difference between the sapwood and the heartwood was generally larger in hardwoods than in softwoods.

Through the survey of trace elements in stems of trees, the element content was revealed to change during heartwood formation. The redistribution of each element was characteristic for tree species. As an attempt to characterize heartwood formation in tree species, content change of five elements (K, Mg, Ca, Mn

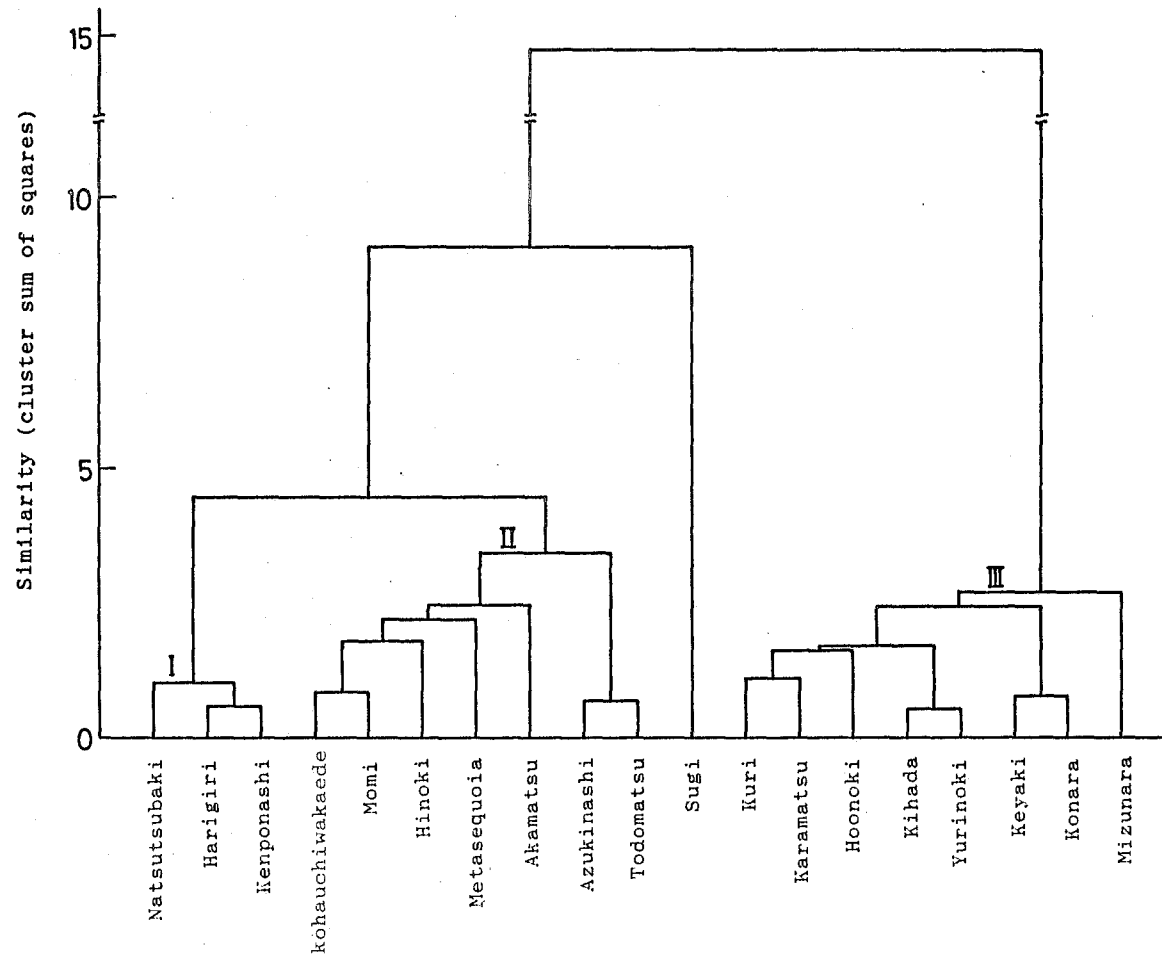


Fig. 3.23 Characterization of tree species by change in element content during heartwood formation.

Note: Variables are ratio of element content (median in heartwood)/(median in sapwood). Elements adopted in calculation are K, Mg, Ca, Mn and Cl.

and Cl) among species was compared by the cluster analysis. These elements belong to different groups in the periodic table, except Mg and Ca, and showed different radial patterns in stems. The result of nineteen species, in which the five elements were accurately determined, is shown as a dendrogram in Fig. 3.23.

In clusters I and II the species, of which element content was larger in heartwood than in sapwood, are included, whereas in cluster III the species, of which element content was larger in the sapwood than in the heartwood, are included. All the softwood species other than karamatsu and sugi were classified to cluster II. In this respect sugi was exceptional among softwood species. Content of most of the elements in sugi was also larger in sapwood than in heartwood, but its difference was much larger than that of other softwoods. Karamatsu was the only species that most elements were rich in sapwood. Cluster III included many hardwood species. Lambert (1981) reported that concentrations of the elements in 90 species in New South Wales were mostly higher in sapwood than in heartwood. This was true in the most of heartwood species in present study, but in softwood species. The result (Fig. 3.23) indicated a different aspect of heartwood formation among the species.

3.4 Summary

In this chapter, trace element distributions in stems of hardwood species were determined, and characteristic in heartwood formation of each species was discussed. The radial distributions of Na and Mn in stem of mizunara were influenced by secondary changes

in tissue more clearly at the breast height than at any other positions in the stem. Therefore, the data at breast height was considered to be appropriate to compare the radial distributions among the hardwood species.

The concentration levels of many elements in hardwoods changed during heartwood formation, and radial distribution patterns were classified into three types.

In Type 1, elements increased outwards around the sapwood-heartwood boundary. The contents of halogens (Cl and Br) and K in most species changed in this manner. In Type 2, most of which were alkaline earth metals, elements decreased outwards around the sapwood-heartwood boundary. In Type 3, the radial pattern of an element had a peak at the sapwood-heartwood boundary. Type 3 included alkali metals, halogens and transition metals, but rarely included alkaline earth metals.

The three types of the radial patterns were element-specific to a certain extent, but not so strongly. In a few species, most of elements were distributed similarly regardless of their chemical properties.

The redistributions of trace elements during heartwood formation reflected the characteristics of the secondary changes among the species. The element content of the most of the softwood species were larger in the heartwood than in the sapwood, whereas that of the hardwood species were larger in the sapwood than in the heartwood.

Conclusions

The major nutrient elements in plants have been studied, and their physiological functions are clarified to a certain extent. However, the functions and significance of other trace elements have not been resolved sufficiently. In particular, little attention has been paid to trace elements in woody plants, although physiological processes which are characteristic of woody plants such as heartwood formation are observed in their stems.

The present study deals with the trace elements in the stems of trees from the two aspects of concerns, the relationship between the trace elements and heartwood formation, and environmental study. The results were summarized as follows:

Several trace elements in the stem of mature sugi were distributed in the radial direction according to the specific patterns, regardless of the tree age and the growing site. Two types of radial patterns were observed; Mn and halogens (Cl and Br) increased outwards from the sapwood-heartwood boundary (Type 1), whereas alkali metals and Mg decreased outwards around the boundary (Type 2). These radial patterns were observed at several stem height in a tree. This change in element concentration suggested that these elements were redistributed during the heartwood formation, i.e., the elements in Type 1 decreased and those in Type 2 increased as heartwood formation proceeded.

The above changes in element content at the sapwood-heartwood boundary observed not only in the radial direction but also in the longitudinal direction

in a stem. Furthermore, the changes in element content in the pith of trees at different growing stages were corresponding to the changes in the radial direction appeared in a stem. This indicated that the physiological changes accompanied with the aging of xylem tissue such as heartwood formation caused the redistribution of element.

Trace elements in the xylem sap of sugi were distributed similarly in the radial direction to those in xylem tissue. The concentration ratio of the xylem sap to the wood substance decreased in the order of

Na, K, Rb, Cl > Mg > Ca, Mn.

It appeared to reflect the mobility in the stem.

The concentrations of trace elements in the stems of softwood and hardwood species changed around the sapwood-heartwood boundary. In addition to the two types of radial distributions observed in a stem of sugi, another radial pattern in which there was a peak at the sapwood-heartwood boundary was observed.

In many case, the elements of similar chemical properties such as halogens or alkali metals had a common radial pattern in a species. However, in some species, most elements were distributed similarly regardless of their chemical properties. Rare earth elements were distributed parallel each other in the radial direction, but not so similarly to other metal elements. Aluminum was detected in many species and was distributed randomly.

Although the concentrations of elements in stem were generally smaller than those in leaves, some species accumulated a particular element in stem comparable to leaves, La in Karamatsu, Al in Himalayan

cedar, Cl in kanakuginoki.

The concentrations of alkali metals in many softwoods were larger in the heartwood than in the sapwood, whereas those of Mn and Cl were larger in the sapwood. On the contrary, in many hardwood species, the concentrations of elements were larger in the sapwood than in the heartwood.

In general, physiological changes, especially heartwood formation, affected more strongly the radial distributions of elements in the stems of trees than the growing condition.

Acknowledgement

The author wishes to express his sincere thanks to Professor Koji Murakami, Department of Wood Science and Technology, Faculty of Agriculture, Kyoto University, for his discussion and suggestion throughout this study.

The author also thanks to Professor Keizo Okamura, Department of Wood Science and Technology, Faculty of Agriculture, Kyoto University, and Professor Goro Iwatsubo, Department of Forestry, Faculty of Agriculture, Kyoto University, for their critical reading of the manuscript and their helpful suggestions.

It is a great pleasure to thank many colleagues, in particular, Mr. Yukio Katayama, Dr. Tadashi Nobuchi, Faculty of Agriculture, Kyoto University, Dr. Yutaka Ishimaru, Faculty of Agriculture, Kyoto Prefectural University, and Dr. Atsushi Aoki, Faculty of Living Science, Kyoto Prefectural University, for discussions and cooperation in element analysis.

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